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**Problems Associated With The Closed Chamber Method Of Soil Gas Flux
Measurements**

by

Benjamin Kweku Sey



A thesis submitted to the Faculty Of Graduate Studies and Research in partial
fulfilment of the requirements for the degree of Master of Science

in

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Faculty of Graduate Studies And Research

The undersigned certify that they have read, and recommend to the faculty of Graduate Studies and Research, for acceptance, a thesis entitled “Problems associated with the closed chamber method of soil gas flux measurements” submitted by Benjamin Kweku Sey in partial fulfillment of the requirements for the degree of Master of Science in Soil Science.

Dedication

To my Sister, Christie, for your selfless commitment to my education

To my nephews and nieces, too many to name, may it be an inspiration to you to explore the depths of knowledge

To my Mom and Dad, for nurturing me through all the turbulent times....

To the almighty God, for the gift of life, and the joy of sharing....

Abstract

The closed chamber method is the most common method used in the estimation of trace gas emissions from soils. I investigated some problems associated with the method in order to improve its efficiency and accuracy.

The first phase of the study involved the development of a diffusion-based model and comparing its performance with the two most common models (linear regression model and Hutchinson and Mosier (H-M) model). Generally, the linear model underestimated fluxes relative to the proposed model and H-M model.

The second phase involved an investigation into the effect of depth of chamber insertion and atmospheric turbulence on the flux estimates. Inserting the chambers deeper was found to increase the headspace concentration build-up.

The third phase studied the effectiveness of the NaOH gas trap used in the static chambers to absorb CO₂ as affected by container size. The performance of the gas traps was generally dependent on the fluxes.

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List of symbols

Symbol	Description
f	Flux ($gcm^{-2} min^{-1}$) $1 gcm^{-2} min^{-1} = 6 \times 10^9 gha^{-1} hr^{-1}$
ρ	Density of gas (gcm^{-3})
v	Flow rate of air in the chamber headspace (cm^3 / min)
t	Time (min)
t_0	Time of chamber deployment (min)
t_1	Time after first sampling time interval (min)
t_2	Time after second sampling time interval (min)
D	Diffusivity of field soil (no unit)
D_0	Diffusivity of reference soil (no unit)
α	Scaling factor (no unit)
I_p	Field chamber headspace concentration function (no unit)
I_0	Reference chamber headspace concentration function (no unit)
V	Chamber headspace volume (cm^3)
A	Soil surface area covered by chamber/ cross-sectional area of chamber (cm^2)
$P_r(t)$	Proportion of gas remaining in the reference chamber as a function of time (no unit)
d	Depth (cm)
C	Chamber headspace concentration [$ppm(V/V)$]
C_H	Chamber headspace concentration (static chambers) [$ppm(V/V)$]
C_t	Chamber headspace concentration at any given time t [$ppm(V/V)$]
C_0	Chamber headspace concentration at time of chamber placement [$ppm(V/V)$]
C_1	Chamber headspace concentration at time t_1 [$ppm(V/V)$]
C_2	Chamber headspace concentration at time t_2 [$ppm(V/V)$]
C_d	Gas concentration at depth d [$ppm(V/V)$]
C_r	Chamber headspace concentration over reference soil

	$[ppm(V / V)]$
C_c	Corrected headspace concentration
	$[ppm(V / V)]$
k	Constant (no unit)

CHAPTER 1. INTRODUCTION

1.1. Introduction

The increasing emissions of greenhouse gases [carbon dioxide (CO_2), nitrous oxide (N_2O) and methane (CH_4)] is currently one of the most important environmental issues because of their potential to alter the atmospheric energy balance (Andrae and Schimel, 1989; Duxbury, 1994, 1995; Hillel, 1998). Some estimates indicate atmospheric concentrations of CO_2 , N_2O and CH_4 are increasing at an annual rate of 0.3%, 0.5% and 0.6% respectively (Watson et al., 1992 as cited by Borken et al., 2000). Current agricultural practices contribute an estimated 25%, 90% and 65% respectively, of the total anthropogenic emissions of CO_2 , N_2O and CH_4 , respectively (Duxbury, 1994, 1995).

1.2. Greenhouse gas sources and sinks in agroecosystems

CO_2 production in agricultural soils is a direct result of soil microbial and rhizosphere respiration (Rochette et al., 1999). N_2O production, on the other hand, results from denitrification in anaerobic soils and nitrification in aerobic soils under oxygen stress (Ball et al., 1999). Methanogenesis (production of CH_4) occurs under anaerobic soil conditions from the action of obligate anaerobic microorganisms through either CO_2 reduction or the process of transmethylation (Hou et al., 2000).

The sources and sinks of greenhouse gases vary between agroecosystems with flooded rice fields and cultivated peatlands as important sources of CH_4 and N_2O but sinks for CO_2 (Mosier et al., 1990; Kasimir-Klemedtsson et al., 1997). In those ecosystems, drainage is a major determinant of whether the land is a source or sink of greenhouse gases. After drainage, decomposition of organic matter increases, CO_2 production increases, and the sites may turn into net sources of C even though there may be a reduction in CH_4 production (Maljanen et al., 2002). Other ecosystems such as forests may serve as a better sink for C than cultivated soils, although research shows that if properly managed, cultivated lands could be important sinks for C (Wang et al., 2002). Carbon sequestration, as this is referred to, strongly depends on

weather and soil conditions, as well as agronomic factors such as crop rotation, fertilizer application, residue treatment and tillage practice (Janzen et al., 1998).

1.3. Production vs. Flux measurements

Gas produced in the soil, given enough time, is emitted to the atmosphere through the primary process of diffusion (Buckingham, 1904; Keen, 1931, Hillel 1998). However, greenhouse gas production is very erratic in soils, varying widely with substrate level and environmental conditions such as temperature and soil moisture, hence making it difficult to measure (Maljanen et al., 2002). As a result, efflux of gases is the common indicator used to measure soil microbial and root activity (Nay et al., 1994). Gas flux measurements help to provide a better picture of the actual quantity of gases released into the atmosphere from soils, as opposed to gas produced in the soil, which may or may not enter the atmosphere. The disadvantage however, of using gas flux estimates as an indicator of soil microbial activity is that, depending on the soil conditions, a time lag may exist between the production and emission which may be substantial (Jury et al., 1982).

1.4. Methods for measuring soil gas fluxes

Traditionally, the chamber method has been the oldest method of measuring CO₂ emission from soils (Bornemann, 1920; Lundegardh, 1921). However, new methods have been developed over the years to achieve this with various degrees of success. These include micrometeorology-based eddy correlation (Nakadai et al., 1993), calculation from the gaseous diffusion theory (Denmead, 1979) and the use of tunable diode lasers (Feng et al., 2000).

Micrometeorology methods also provide large-area average gas flux measurements. However, the “footprint” area of the measurements is uncertain and can be quite variable. In addition, this method, although commonly used for CO₂ fluxes, has limited application for N₂O and CH₄ emissions. Calculating the flux and production from diffusion theory and soil concentration profile is one promising area. However, where the gas production is transitory, or where production is too close to the surface, problems arise due to the difficulty in measuring the concentration

gradient (Denmead, 1979). Accurately determining the diffusion coefficient of the soil is another challenge, which is difficult to overcome due to the high variability of diffusivity under field conditions (Denmead, 1979). The use of tunable diode lasers can provide measurements of gas fluxes averaged over large areas but are less sensitive to the spatial variability of the soil gas fluxes. In addition, the cost involved in the use of the method is limiting and their reliability not proven (Feng et al., 2000).

The soil chamber method remains the most common method used in the measurement of gas fluxes from soils and other porous media (Nay et al., 1994). This is because it has the advantage over the other methods of low cost and ease of use (Feng et al., 2000). There are two types of soil chambers; those with forced airflow, referred to as the open chambers and those with either a closed loop of circulation or no forced circulation, referred to as the closed chambers (Hutchinson and Mosier, 1981).

1.5. Closed chamber method

This method uses an inverted chamber covering the soil surface. The most commonly used chambers are cylindrical, although rectangular chambers are also used. Various depths of insertion used in the past by different researchers range from 0.5 cm (Nay and Bormann, 2000) to 10 cm (Bajracharya et al., 2000). This is in an attempt to provide a better seal against leakage around the edges of the chamber. Many closed chamber studies also employ soil collars to reduce the lateral diffusion of gases from the chamber headspace and improve the seal (Chang et al., 1998).

Once the chamber covers the soil surface, soil gas emission leads to an accumulation of gas in the chamber. This concentration build-up as measured is used to determine flux. Unlike open chambers, the closed chambers are more sensitive to smaller fluxes since gases emitted by the soil into these chambers are not constantly diluted (Hutchinson and Mosier, 1981). There are two types of closed chambers. The dynamic closed chamber method and the static closed chambers.

In the dynamic method, the headspace gas concentration is measured at specific intervals for the duration of the experiment. Soil gas flux is then calculated from the increase in the gas concentration in the chamber headspace. Gas concentration in the

chamber headspace, for this method, is usually monitored with infrared gas analyzers (IRGA) (Nay et al., 1994; Hashimoto, 2001) or by periodic sampling with syringes for subsequent analyses using gas chromatography (Chang et al., 1998).

Theoretically, the gas flux can only be calculated from the rate of concentration increase in the chamber at $t \rightarrow 0$, or at the time of chamber placement. As gas concentration in the chamber increases there is a distortion in the soil gas concentration gradient. This affects the rate of further gas accumulation in the chamber. As a result, the relationship between the gas concentration in the chamber and the time is non-linear (Hutchinson and Mosier, 1981; Denmead, 1979). The non-linearity of gas concentration in the chamber can affect the values of the estimated soil gas flux.

In the static method, the cumulative concentration of the gas in the soil chamber headspace is measured once at the end of the experiment to determine the flux, usually by linear extrapolation. In this method, chemical absorbents are often employed to absorb the gas emitted into the chamber headspace over the sampling period (Hutchinson and Rochette, 2003). In the case of CO₂ gas fluxes, the measurement involves the placement of a chemical traps such as NaOH (Franzluebbers et al., 2000), KOH (Franzluebbers et al., 2002) or soda lime pellets (Nay et al., 1994) in the chamber headspace. The amount of gas absorbed by the gas trap is later determined by chemical analyses and the flux calculated as an average over the period of sampling. Theoretically, this method can provide measurements of average gas flux over long periods. This avoids issues of temporal (diurnal) variations in soil gas flux. However, serious problems can arise with the use of this method. The low effectiveness of absorption of the gas traps under high emissions is a great source of error (Rochette et al., 1992; Hutchinson and Rochette, 2003). When soil gas flux is high, static chambers tend to underestimate gaseous flux from soil surfaces because of the alteration of the micro-climate, air pressure differences inside and outside the chamber and reduction of the turbulent air flow above the soil surface (Hutchinson and Livingston, 1993; Rochette et al., 1992). Under low flux, before the placement of the soil cover, the boundary layer of air in contact with the soil surface contains CO₂ at a lower concentration than the soil air and this concentration gradient drives the

diffusive process. After the placement of the covers however, the CO₂ in the chamber air is quickly absorbed. The concentration gradient of the CO₂ increases leading to an increase in the flux into the chamber greater than the natural rate. The flux measurement as a result is often exaggerated (Hutchinson and Rochette, 2003). Under high emissions, the chemical traps absorb gas from the chamber at a rate that is smaller than the rate of emission of the gas into the chamber. As time proceeds, the CO₂ concentration builds up in the chamber and the flux reduces as a result. Readjustment of the CO₂ in the soil profile occurs as the headspace concentration building up. This results in lateral diffusion beneath the chamber walls and an underestimation of flux (Hutchinson and Rochette, 2003).

1.6. Open chamber method

In open chambers, the headspace gas is continually diluted over the sampling period (Hutchinson and Mosier, 1981). This mixing of the enclosed air with ambient air maintains the headspace gas concentration in an open chamber similar to those observed in the undisturbed field. However, the open chamber method can be unreliable (Denmead, 1979). This is because the pressure deficit between the chamber headspace and the atmosphere can lead to mass flow of gases into the chamber headspace. Denmead (1979) observed that very minute pressure deficits created in the open chambers resulted in N₂O fluxes that were several times larger than diffusive flow, thus producing spuriously high estimates of flux in the field. Similarly, Kanemasu et al. (1974), in comparing the CO₂ fluxes from soils measured by blowing vs. drawing air through an open chamber (pressure differentials of +2.5 Pa and -1 Pa from ambient, respectively), found that measured CO₂ fluxes differed by nearly an order of magnitude. In addition, the continual mixing with ambient air makes the method not very sensitive to smaller fluxes. Hutchinson and Mosier (1981) reported that a substantial percentage of N₂O fluxes measured periodically using a closed chamber was below the open chamber detection limits of 0.06 and 0.16 g N ha⁻¹ hour⁻¹ as reported by Denmead (1979) and Ryden et al. (1978), respectively.

1.7. Chamber mixing and flux

Many studies have assumed a uniform mixing in the chamber headspace (Mathias et al., 1978; Hutchinson and Mosier, 1981). However, simulations by Healy et al., (1996) showed that under field conditions, the chamber headspace may not be completely mixed. The build-up in concentration in the chamber was linear at the center and exponential at the edges. In addition, the concentration at the center of the chamber headspace increased to a higher level than the concentration at the edge. This finding has particular importance in relation to the type of sampling method used. In the dynamic chamber method, where syringes are used, the implications of this may be an under-estimation of the flux as observed in controlled laboratory experiments by Nay et al. (1994). They found that the dynamic method under-estimated flux by as much as 15% when syringes were used to sample gases from the chamber periodically. In the static chambers, where gas traps are used, the position of the traps in the chamber may be critical to the reliability of the flux estimates.

1.8. Issue of non-linearity

The buildup of gas concentration in the chamber and the resulting reduction of the measured flux with time in the closed chamber method has been the focus of criticism of the closed chamber system. This is because, unlike the open chamber system, a steady state in the soil is never attained (Denmead, 1979). There is continuous change in the concentration in the chamber air and hence a continuous readjustment of the gas concentration in the soil profile after chamber placement (Denmead, 1979).

In a classical sense, before the placement of the cover, the flux from the soil is driven mostly by diffusion. The soil is at steady state and the rate of production equals the rate of diffusion. The concentration of gas in the soil therefore remains fairly constant with time. In the initial stages after the placement of the soil cover, the flux rate is approximately equal to that of the uncovered soil and the concentration of gas in the soil is approximately equal to the concentration before the placement of the chamber. As the concentration builds up in the chamber with time, however, there is a readjustment of the gas concentration in the soil profile and the flux of gas into the chamber reduces continuously with time (Healy et al., 1996). Because gas diffusion is

a slow process, the distortion of the concentration gradient initially occurs only very near the soil surface and then with time the distortion slowly propagates downwards (Healy et al., 1996). At that stage, the flux falls below the production rate and leakage of the gas around the edges of the chamber might occur. As this trend proceeds, there is increased occurrence of lateral diffusion of gases in the lower soil profiles. As a result, instead of a constant rate of concentration build-up in the chamber headspace, which is expected in the ideal case, there is a continuously declining rate of gas concentration build-up, and hence the estimated flux with sampling time. This problem needs to be addressed in order to obtain accurate measurements of the flux.

1.9. Non-linear models

A number of researchers in the past have attempted to explain the non-linearity problem in the closed chamber using computer simulation models and mathematical models. The most commonly used non-linear model is the Hutchinson and Mosier (H-M) model (1981). The assumptions of that model were as follows:

1. At a depth, d , close to the upper limits of the production zone, the concentration of CO_2 in the soil profile is assumed to be constant and not affected by the placement of the chamber
2. The flux into the chamber headspace is proportional to the concentration difference between the headspace (same as soil surface concentration) and the fixed concentration at the depth, d .
3. The gas concentration build-up in the soil is negligible after the placement of the chamber.

Although this model has been used extensively in many studies, the assumption of production occurring at a certain fixed depth as compared to a more spread zone of production is not realistic. In addition, the notion that exchange of gases across the soil-atmosphere boundary is explained by a one-dimensional diffusion equation has not been independently evaluated (Healy et al., 1996). Although, other non-linear models have been developed, such as the stochastic diffusion model by Pedersen et al. (2001) and the diffusion-based model by Feng et al. (2000), their accuracy and reliability have not been independently confirmed. Currently therefore, the two most

common models used in closed chamber studies are the linear regression models and the Hutchinson and Mosier (H-M) model (Pedersen et al., 2001).

1.10. Justification for study

To this date, there has been limited research done on the factors that influence the accuracy of the soil chamber method. In addition, a comprehensive evaluation of the models used in flux estimates is needed. Although the linear model and the H-M models are the most widely used model for trace gas flux from soils, there has not been much work in comparing flux estimates from the two models. One area where research is especially lacking is the effect of the depth of insertion of the chamber on the measured flux. Increasing the depth of insertion was reported by Ryden et al. (1978) as helping to decrease the extent of mass flow in the open chamber system. Also in cases where continuous monitoring of the chamber headspace concentration is not practical, the best sampling time to use as well as the minimum number of gas samples needed has not been adequately studied. The objectives of this study therefore were:

1. To quantify the effect of depth of insertion and collar size on the flux estimates.
2. To quantify the impact of physical factors such as wind dynamics on the flux estimates.
3. To investigate the effectiveness of the gas traps in both lab and field trials and the influence of factors such as container size on gas absorption efficiency.
4. To test the performance of the linear and H-M models in estimating CO₂ flux and to develop a model that is easier and more reliable to use under field conditions for flux estimation.

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CHAPTER 2. MODELLING FLUXES IN CLOSED CHAMBERS

2.1. INTRODUCTION

Transport of gases in soils is mostly by gas diffusion and mass flow (Hashimoto and Suzuki, 2002). However, the placement of the soil chamber on the soil surface alters the dynamics of soil gas flux. This change is the basis of the problem of non-linearity in closed chambers. The decline in the rate of gas concentration build-up into the chamber headspace and the resulting reduction in the flux is the main criticism for the closed chamber system. Unlike the open system, a steady state in the soil is never attained (Denmead, 1979). There is continuous change in the concentration in the chamber air and hence a continuous readjustment of concentration within the soil profile (Denmead, 1979).

Linear regression models may be useful in situations such as in short sampling periods where non-linearity is assumed to be insignificant or in cases of testing the model's goodness of fit to the concentration data (Anthony et al., 1995). However, application of linear models to measured flux may seriously underestimate the undisturbed flux (Hutchinson and Livingston, 1993). Some researchers have however attempted to overcome this problem by developing diffusion-based exponential models. Examples of these include the Hutchinson and Mosier (H-M) model (1981), the Feng et al. model (2000) and the Pederson et al. (2001) stochastic model. However, the two most widely used models for estimation of trace gas emissions in chamber methods are the linear model and the H-M model.

2.2. THEORY

2.2.1. The linear model

The linear model is the most simplistic model used in flux estimation. It assumes a constant rate of gas build-up in the soil chamber. For the closed chamber system, flux can be estimated directly from the build-up of gas concentration in the chamber headspace, assuming a constant rate of concentration build-up. For a chamber headspace volume, V covering a surface area of A , the flux, f can be estimated as:

$$f = V(C_t - C_0) / At \quad [1]$$

where C_t is the headspace concentration after a time, t and C_0 is the initial headspace concentration (Hutchinson and Mosier, 1981). In the open chambers, a variation of this model is used:

$$f = (\rho v / A) \Delta C \quad [2]$$

Where ρ is density of gas, v is the flow rate maintained by the pumps used to drive the open system air circulation and ΔC is the concentration differential between the inlet and outlet ports of the chamber. Denmead (1979) in a study of nitrous oxide emissions from grass sward utilized this model to estimate the fluxes of N_2O .

However, complications arise when it comes to the issue of sample time and its drastic impact on the accuracy of the flux estimates. This is due to the effect of the non-linearity of concentration build-up in the chamber as observed in many studies (Hutchinson and Mosier, 1981; Denmead, 1979; Healy et al., 1996). The chamber placement causes a time-dependent distortion of the concentration gradients that drive gas diffusions, leading to increasingly lower influx of gas into the soil chamber with time (Healy et al., 1996). As a result, the linear models, when compared to diffusion-based models such as the H-M models, consistently underestimate the flux (Pedersen et al., 2001; Anthony et al., 1995; Healy et al., 1996; Petersen, 1999).

2.2.2. Non-linear models - The H-M model (1981)

This is an exponential model based on diffusion theory and was proposed to account for the decrease in the flux due to concentration build-up in the chambers. For a closed chamber with internal volume, V , and initial gas concentration, C_0 , placed on the soil surface area, A , after a time interval, t , if gaseous flux into the chamber is assumed to be linear, the gaseous flux from the soil can be estimated by equation [1]. However, this estimate of the flux does not account for the decrease in the flux due to the concentration build-up in the chamber. In order to account for this decrease in the flux, the model assumes the following (Hutchinson and Mosier, 1981):

1. The soil is at steady state before the measurements are made.

2. The concentration, C_s , at the soil surface is the same as the concentration C measured in the chamber headspace.
3. At a depth, d , close to the upper limit of production zone, there is a constant concentration, C_d , which is not affected by the changes in the headspace concentration during the relatively short period of measurement.
4. Gas concentration increases linearly with depth between the soil surface and the depth, d .

Hutchinson and Mosier (1981) developed the model as follows:

Given that the quantity of gas that accumulates in the enclosure, q , in a time, t , the surface gas flux, f , from Fick's law can be approximated as,

$$f = (1/A)(dq/dt) = D(C_d - C_s)/d \quad [3]$$

where D is the gaseous diffusion coefficient or diffusivity in the soil. For a closed chamber,

$$dq = VdC \text{ and } C_s = C \quad [4]$$

where V is volume of the chamber and C is gas concentration in the chamber.

According to the assumptions, $C = C_s$. Combining equations [3] and [4], separating the variables and integrating yields

$$\ln[(C_d - C_0)/(C_d - C_t)] = ADt/Vd \quad [5]$$

Solving for D , evaluated at time t_1 , when the headspace gas concentration is C_1 yields

$$D = (Vd / At_1) \ln[(C_d - C_t)/(C_d - C_1)] \quad [6]$$

Substituting [6] into [3] evaluated at time t_0 , initial flux f_0 can be defined as

$$f_0 = \frac{D(C_d - C_0)}{d} = \frac{V(C_d - C_0)}{At_1} \ln \left[\frac{C_d - C_0}{C_d - C_1} \right] \quad [7]$$

Hutchinson and Mosier (1981) stated that, if $t_2 = 2t_1$, it follows from the assumptions that the ratio of the headspace concentration increase to the initial soil concentration gradient must be the same for both measurement periods, or:

$$\frac{(C_1 - C_0)}{(C_d - C_0)} = \frac{(C_2 - C_1)}{(C_d - C_1)} \quad [8]$$

Hence, the concentration gradient between the soil and headspace was assumed to be the same for both measurement periods. Solving for C_d yields

$$C_d = (C_2 C_0 - C_1^2) / (C_2 - 2C_1 + C_0) \quad [9]$$

Combining [7] with [9] gives:

$$f_o = \frac{V(C_1 - C_0)^2}{At_1(2C_1 - C_2 - C_0)} \ln \left[\frac{C_1 - C_0}{C_2 - C_1} \right] \quad [10]$$

This is the estimate for the initial gas flux at the time of gas chamber placement.

The H-M model, although an improvement over the linear model, has its drawbacks. Firstly, the model assumed a constant concentration at a depth close to the upper limit of the production zone after the placement of the soil cover, which is not realistic because a steady state in closed systems is hard to achieve due to the constant readjustment of gas concentration in the soil profile. The gas concentration of the soil in the upper zone of production is most likely under a state of constant readjustment and does not stay constant as assumed in the H-M model.

Secondly, the gas concentration in the soil varies with the time of day and ambient temperature. The model assumes a constant rate of production, which could be a source of error in extended sampling times due to the high variability in the flux over time under field conditions.

Thirdly, the method involves the use of three measurements of headspace concentrations taken at equal time intervals with the assumption that the ratio of headspace concentration increase to the initial soil concentration gradient must be the same for both measurement periods. In reality however, the concentration gradient in the soil may decline after the placement of the chamber resulting in the decline of fluxes into the chamber headspace.

The assumption was that:

$$\frac{(C_1 - C_0)}{(C_2 - C_1)} > 1 \quad [11]$$

where C_0 , C_1 and C_2 are the concentrations at times t_0 , t_1 , and t_2 , respectively. The problem with this assumption is that although it makes sense theoretically, field measurements may follow a very erratic pattern. For example, Anthony et al. (1995) applied the Hutchinson and Mosier (1981) model 2224 times and reported failure in 45% of the cases because equation [11] was not supported by the data obtained (as cited by Pedersen et al., 2001). In those cases, the gas build-up into the chamber headspace after placement of the chambers did not follow the expected exponential pattern as assumed in the H-M model. The H-M model takes no account of the concentration build-up in the soil zone between the surface and the depth d after the chamber placement. It assumes concentration to be constant at depth $z = d$ and that concentration at $z = 0$ (surface) increases during the duration of the measurement. However, since concentration is changing at the soil surface and production is assumed constant, it is logical to assume an accumulation in the soil profile between the soil surface and $z = d$.

2.2.3. The proposed model

The model is based on the hypothesis that the gas movement in the soil-chamber system is mostly by diffusion. As the concentration in the chamber headspace builds up, a concentration gradient develops between the chamber headspace and the surrounding atmosphere. This leads to a diffusive flux between chamber headspace and the surrounding atmosphere which is responsible for the non-linearity of the soil chamber method. The diffusion process is a function of the soil gas diffusivity, the headspace volume, the size, shape, and the insertion depth of the chamber.

As in the H-M model, the assumptions are that the soil is at a steady state before the deployment of the chamber and that the chamber air is well mixed, so that the gas concentration in the chamber headspace is the same as the gas concentration at the soil surface within the chamber.

Our problem is to find a solution for the non-linear gas concentration buildup into the chamber headspace. Gas movement from soil into the chamber is dominated by the diffusion process. The movement of gas molecules by diffusion results from the random motion of molecules. For a soil where the gas diffusivity is constant, one

basic characteristic of the diffusion process is that the movement of one molecule is not affected by the presence of other molecules in the system. In the mathematical terminology, the differential equation describing the diffusion process is said to be linear as defined in equation [11].

Consider a soil that is at steady state before the deployment of the chamber. Gas molecules are being produced in the soil and moving toward the soil surface by diffusion. For individual molecules undergoing this process, the deployment of the chamber and the change in the gas concentration in the chamber headspace has no effect on its movement. Thus, after the deployment of the chamber, the gas molecules being produced in the soil will continue to escape from the soil surface into the chamber headspace at a constant flux, f .

However, the molecules that have entered the chamber headspace may, in the reverse direction, move into the soil by the same diffusion process and eventually escape from the soil surface outside the chamber into the atmosphere.

Assuming a unit quantity of gas molecules are injected into the chamber headspace at $t = 0$. As time progresses, some of these molecules will move into the soil and eventually find their way to the atmosphere outside the chamber. The proportion of the gas molecules that remain in the chamber headspace decreases with time. The fraction of the gas molecules that remain in the chamber headspace, as a function of time, can be found by solving the diffusion for the chamber system. Alternatively, it can be found experimentally.

For experimental determination, the chamber can be inserted into a reference soil with zero rate of target gas production in the laboratory and then allowed to equilibrate. The gas diffusivity of this soil is D_0 . At $t = 0$, a known quantity of gas can be injected into the chamber and the change in the gas concentration in the chamber monitored. Assuming that the gas concentration in the atmosphere, and the initial equilibrium concentration in the chamber headspace is C_{ar} . After injection, the gas concentration in the chamber headspace is raised instantaneously to C_{ir} . The proportion of the injected gas that remain in the chamber head space, p as a function of time, is then

$$p_r(t) = \frac{C_r(t) - C_{ar}}{C_{ir} - C_{ar}} \quad [12]$$

where $C_r(t)$ is gas concentration in the chamber headspace as a function of time.

At this point, a clarification on the symbols is necessary. The subscripts used in the development of the proposed model are as follows. The subscript ‘ r ’ is used to refer to the reference soil used in the laboratory determination. For the field soil measurements, the subscript ‘ p ’ is used. The subscript ‘ i ’ refers to initial, thus C_{ir} is the initial concentration in reference soil measurement. The subscript ‘ a ’ refers to background or equilibrium values.

Theoretically, ignoring the interaction of the chamber walls and diffusion on flux, the total concentration of gas in the chamber headspace at any given time, or correct concentration, C_c can be defined by the linear relationship (Hutchinson and Mosier, 1981):

$$C_c = fAt/V \quad [13]$$

However, under normal circumstance, if a constant gas flux, f , is entering the chamber, the gas concentration in the chamber headspace at any given time is the summation of the gas that has entered chamber previously but has remained in the chamber. This is a product of the concentration as expected under linear conditions and the proportion of the gas that is expected to remain in the chamber headspace, after factoring in diffusion out of the chamber headspace. Thus, the chamber headspace concentration will be defined by the relationship:

$$C_r(t) - C_a = \frac{fA}{V} \int_0^t p_r(t)dt = \frac{fA}{V} I_0(t) \quad [14]$$

where the integral

$$I_0(t) = \int_0^t p_r(t)dt \quad [15]$$

is the *reference chamber headspace gas concentration function*. It is identical to the concentration buildup in the chamber under the constant flux

$$\frac{fA}{V} = 1 \quad [16]$$

Our problem of finding a mathematical solution for the non-linear gas concentration buildup into the chamber headspace, from a soil with unknown production rate, is then converted into finding the non-linear gas concentration buildup in a chamber inserted into a soil with zero rate of gas production while receiving a constant rate of gas injection in to the chamber headspace.

The function $I_0(t)$ is dependent on soil gas diffusivity, and the geometry of the chamber, i.e., shape, size and the depth of insertion. This function can be determined experimentally or mathematically by solving the diffusion equation, for a given chamber and a reference soil with gas diffusivity D_0 .

The soil gas diffusivity is a function of soil properties, such as and water content. In addition, in field soils near the soil surface, air pressure fluctuations induced by wind will also produce additional dispersion of soil gas, which, mathematically, can be expressed as the increased apparent diffusivity. As a result, the apparent gas diffusivity, D_p , that is applicable for chamber measurements is dependent not only on soil conditions but also on wind and the penetration of wind induced air pressure fluctuations in the soil. An *a priori* measurement or calculation of an accurate value of D_p applicable for gas flux measurements by the chamber method is thus not practical.

One characteristic of the diffusion process is that for fixed system geometry, the rate of the process is directly proportional to diffusivity (Hillel, 1998). Thus, the reference chamber headspace concentration function, determined for a soil with reference diffusivity, D_0 , may be scaled to the field soil, with a soil diffusivity D_p . For the field soil, we thus have

$$I_p(t) = I_0\left(t \frac{D_p}{D_0}\right) = I_0(\alpha t) \quad [17]$$

where $\alpha = D_p / D_0$ is a scaling factor that corrects for differences in diffusivity between the reference soil and field soil by adjusting the time t for calculating the

I_p from the I_0 . This equation states that if the field soil under consideration has the same diffusivity as that of the reference soil, $\alpha = 1$, $I_p(t) = I_0(t)$. If, on the other hand, the diffusivity for the field soil is $1/2$ the diffusivity of the reference soil, $\alpha = 0.5$, we would have $I_p(t) = I_0(0.5t)$. This means that the diffusion process takes 1 hour in the field soil, the same process would only take 0.5 hour in the reference soil.

Equation [14] defines the non-linear conditions in the field while equation [13] defines the ideal linear condition, or corrected concentration, C_c . In order to correct for non-linearity, we divide equation [14] by a correction factor, $N(t)$ defined as:

$$N(t) = I_p(t)/t = I_0(\alpha t)/t \quad [18]$$

The corrected concentration for chamber measurements in the field, can be defined by combining equations [14] and [16]:

$$C_c(t) = \frac{C_p(t) - C_a}{N(t)} = \frac{fA}{V} t \quad [19]$$

Where C_c is the corrected concentration, the concentration where the non-linearity of the concentration in the chamber headspace has been corrected. It is a linear function of time and soil gas flux, as in the linear model. Since I_0 can be determined in the laboratory for a particular chamber, the only unknown is the scaling factor, α .

The scaling factor can be determined in two ways. First, one can utilize the non-linear regression method. If the correct value of α is used, plotting C_c against t would result in a straight line with zero intercept and a slope equals to fA/V . Thus, one can adjust the value of α until the linear relationship between C_c and t has the highest R^2 . The resulting α value will be the estimated scaling factor and the slope of the linear relationship can then be used to calculate the soil gas flux, f . This method can be used to analyze data containing any number of measurements ($n \geq 2$) at

arbitrary time intervals. This method is particularly useful when the measured chamber concentration exhibits large fluctuations.

An alternative method can be used when the gas concentration in the chamber is measured at constant time intervals. Suppose that the gas concentration in the chamber was measured at $t = 0$, t_1 , and t_2 , where $t_2 = 2t_1$, t being time after the deployment of the chamber. According to equation [17] and [19], we have

$$\frac{C_{c2}}{C_{c1}} = \frac{C_2 - C_a}{C_1 - C_a} * \frac{I_0\left(\frac{1}{2}\alpha t_2\right) / \left(\frac{1}{2}t_2\right)}{I_0(\alpha t_2) / t_2} = \frac{1}{2} \quad [20]$$

Which can be simplified to

$$\frac{I_0(\alpha t_2)}{2I_0(\alpha t_2 / 2)} = \frac{(C_2 - C_a)}{2(C_1 - C_a)} \leq 1 \quad [21]$$

where $I_0(t)/2I_0(t/2)$ is referred to as the non-linearity factor. It is worth noting that the left hand side of equation [21] deals with data that is solely derived from diffusion experiments with a reference soil in the laboratory while the right hand side represents actual concentrations measured on the field. With $I_0(t)$ determined experimentally in the laboratory, or through numerical solution of the diffusion equation, one can plot the non-linearity factor $I_0(t)/2I_0(t/2)$ as a function of t . In a field experiment, once we have determined $\frac{(C_2 - C_a)}{2(C_1 - C_a)}$ for some arbitrary times

$t_2 = 2t_1$, then we can find from the plot of $I_0(t)/2I_0(t/2)$ some t^* at which

$$\frac{I_0(t^*)}{2I_0(t^*/2)} = \frac{(C_2 - C_a)}{2(C_1 - C_a)} \quad [22]$$

The scaling factor is then calculated as

$$\alpha = t^* / t_2 \quad [23]$$

This scaling factor helps to adjust for differences in the diffusivity between the reference soil and the field soil. In order to determine which integral to use for any data point, multiply the sampling time in the field (in this case t_2) by the scaling

factor, α , to determine which Integral, I_0 , to use in the relationship expressed in equation [17] and then finally in equation [19] to obtain the corrected concentration at that particular sampling time, t_2 .

At this point, the correction factor can be applied to the measured chamber concentration at any time, t . A plot of the corrected concentration C_c against t yields a straight line with zero intercept. The slope of the curve can then be used to calculate the soil gas flux.

If the chamber concentration has been monitored continuously, then, theoretically any measurement can be used as C_2 to determine the scaling factor. A validation of the model is achieved if the resulting scaling factor and the soil gas flux is independent of the particular measurements used to derive the scaling factor. For this method, the minimum number of measurements is obviously two, in addition to the determination of background gas concentration C_a .

2.3. MATERIALS AND METHODS

2.3.1. Laboratory experiments

Diffusion experiments were conducted in a sand box (40 cm deep, 50 cm wide). The size of the sand box was selected so that the 'zone of influence' of the chamber was kept well away from the walls. The reference soil used was clean sterilized coarse-textured sand with a bulk density of 1.77 Mg/m^3 . Carbon dioxide was chosen as the subject gas because of the availability of the means of monitoring it. The carbon dioxide concentration was monitored using the LI-6400 infrared gas analyzer (LICOR, Lincoln, Nebraska, U.S.A.). The results are expected to apply to all other non-adsorbing soil gas flux measurements. The closed chamber dynamic method was employed in this study. The headspace volume of the chamber was 787.7 cm^3 with a cross-sectional area of 71.6 cm^2 . The soil chamber had a diameter of 10 cm. Instantaneous flux of CO_2 in the chamber headspace in the diffusion experiments was achieved by injecting 3000 ppm of CO_2 through the inlet tubing of the IRGA. The decrease in the CO_2 concentration in the chamber, as a result of the diffusion from the

chamber, through sand and eventually to the outside atmosphere, was monitored continuously. The IRGA was configured to take measurements of CO₂ concentration in the chamber headspace every minute for the duration of the experiments.

2.3.2. Field experiments

All field experiments were conducted at the University of Alberta Research Station at Ellerslie, Alberta in the summer of 2002 (see Appendix B for site description). All experiments were conducted on a no-till plot with no vegetation in order to eliminate interference of photosynthetic uptake of CO₂ gas with soil respiratory CO₂ flux. In order to vary the depth of insertion while keeping the headspace concentration fixed, five extension cylinders or collars were fabricated to fit tightly on the base of the chambers. The internal diameter of the cylinders was approximately the same as the chamber (10 cm). The extension cylinders were cut to different heights (5 cm, 7 cm, 9 cm, 11 cm, 13 cm) with a 2 cm allowance to create an overlap and seal between the chamber and the extension cylinders (see Fig 2.1). All measurements for were done in the morning to early afternoon to eliminate the variations in fluxes between days and reduce the effect of the diurnal variations. The order in which the experiments were conducted for the 2 replicates was randomized.

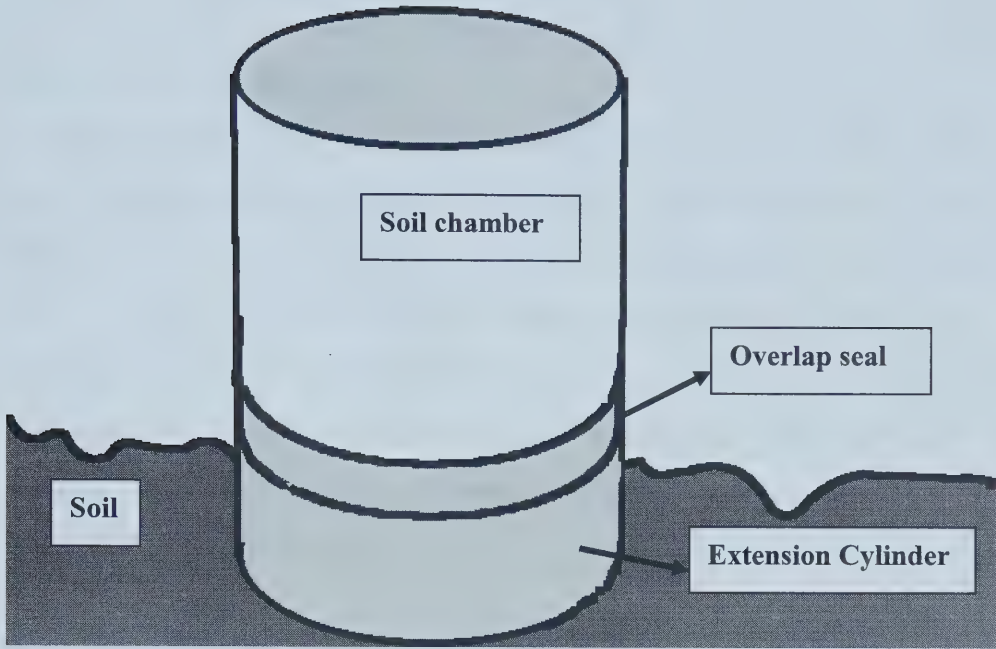


Fig. 2.1. Schematic diagram of soil chambers and extension cylinders

Headspace concentration was measured and logged by the IRGA at 1 minute intervals for 60 minutes for each experiment. Care was taken in the insertion of the chamber and taking of measurements not to disturb the soil profile. This was done to eliminate the chances of causing a sudden spur in the flux as reported in studies by Otten et al. (2000). The effect of depth of insertion on the model estimates was analyzed from the data obtained from these series of experiments.

2.3.3. Testing the fixed concentration assumption of the H-M Model

One of the principal assumptions of the H-M model (1981) is that at a certain depth, d , close to the upper limits of the production zone, the concentration of CO_2 in the soil profile, C_d is not affected by the placement of the closed chamber on the soil surface. In order to test the validity of this assumption, the following procedure was used:

From the H-M, model,

$$\ln[(C_d - C_0)/(C_d - C_i)] = ADt/Vd \quad [24]$$

Assuming D or diffusivity is fixed

$$\ln[(C_d - C_0)/(C_d - C_t)] = kt \quad [25]$$

where $k = AD / Vd$, is a constant.

If the Hutchinson model is true, a plot of $\ln[(C_d - C_0)/(C_d - C_t)]$ against t should yield a straight line with an intercept of zero. Also, C_d is not expected to vary with factors such as the depth of insertion of the chamber in the soil, nor with the sampling time. To estimate C_d , a non-linear least square regression method was used to fit equation [25] to the measured chamber concentration C_t with k and C_d being the fit parameters. The C_d value that allow for the best fit of equation [25] to the measured chamber concentration was used as an estimate of the fixed soil concentration as suggested by the H-M model.

2.3.4. Comparing flux estimates from linear, H-M and proposed models

Linear model flux estimates were derived from the measurements of concentration using the linear relationship:

$$f = V(C_t - C_0) / At \quad [26]$$

Where V is the volume of the chamber headspace, A is the area of soil surface covered by chamber C_t is the headspace concentration after a time, t , and C_0 is the initial headspace concentration (Hutchinson and Mosier, 1981). The flux estimates were then compared with that obtained from the H-M model and the proposed model using the same data set.

2.4. RESULTS AND DISCUSSION

2.4.1. Depth of insertion and the fixed concentration assumption of the H-M model

Fig 2.2 shows the variation in the calculated concentration at the fixed depth of the upper limit of the production zone for the H-M model with varying depth of insertion of the chamber.

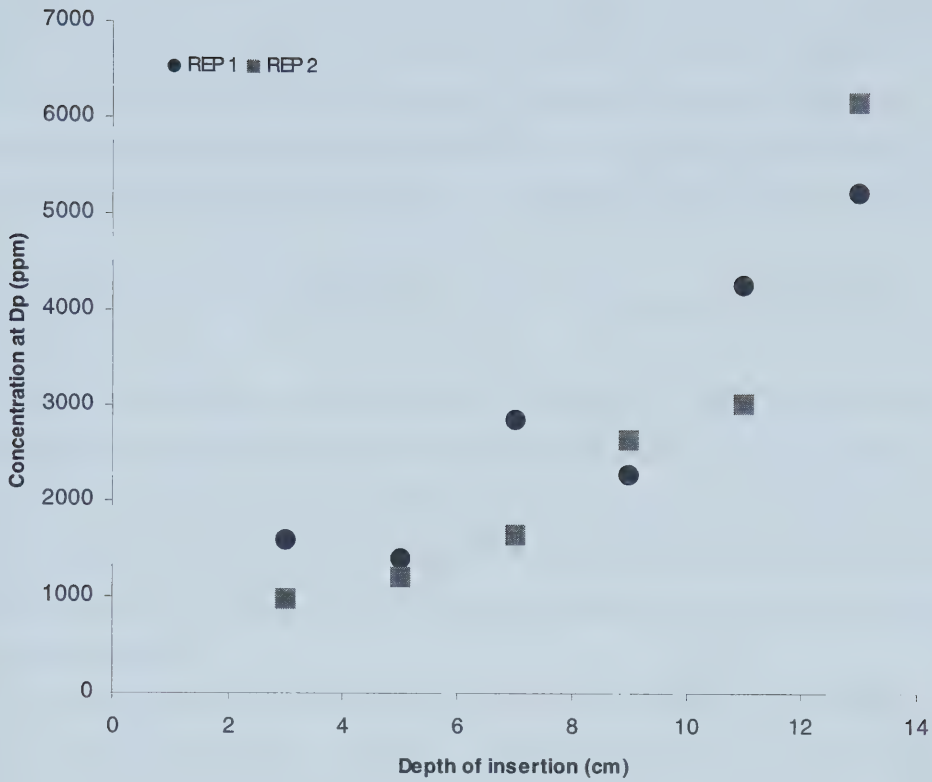


Fig. 2.2. Effect of depth of insertion on calculated C_d for the H-M model.

The fixed-depth concentration increased with the depth of insertion. At 13 cm depth of insertion, it was 5 times that at 3 cm depth. This is clearly contrary to the basic assumption of the H-M model where the fixed concentration theory is one of the principle assumptions (Hutchinson and Mosier, 1981).

The results show a clear pattern that the calculated concentration at the fixed depth of the H-M model increases with an increase in the depth of insertion. Contrary to the assumption that, closer to the upper limits of the production zone in a soil that is not affected by the presence of the cover in the duration of the experiment, the results show that the depth of insertion of the chamber could have a significant effect on the calculated concentration at this depth. This suggests that one of the principal assumptions by the H-M model is flawed.

The results are similar to that obtained from the study by Pederson et al. (2001). In their tests of the H-M model, they reported very variable values for d (depth of constant concentration). They concluded that it is not the not-so-well defined boundary condition but, rather, a vertical distribution of production and consumption that reflects the specific combination of environmental variables at each depth.

2.4.2. Measurement time intervals and effects on flux estimates of the H-M model

One of the advantages of the H-M model is the simplicity of measurements. The model allows for only 3 measurements of concentration to be made at equal time intervals (Hutchinson and Mosier, 1981). However, there is no time interval recommended for use in this model. The flux estimates obtained from using different time intervals (5, 10, 15, 20, 25 minutes) from the model for 5 series of measurements are shown in Fig 2.3.

The results generally show a fluctuation in the estimated flux; however, they do not follow a clear trend. Generally, fluctuations in the flux estimates were small, being more consistent at sampling intervals >15 min. From the results one may assume that although the H-M model has no recommendations for the specific sampling interval to be used, time intervals of >15 minutes seem to reduce the variability of the flux estimates, for the chamber used in this study.

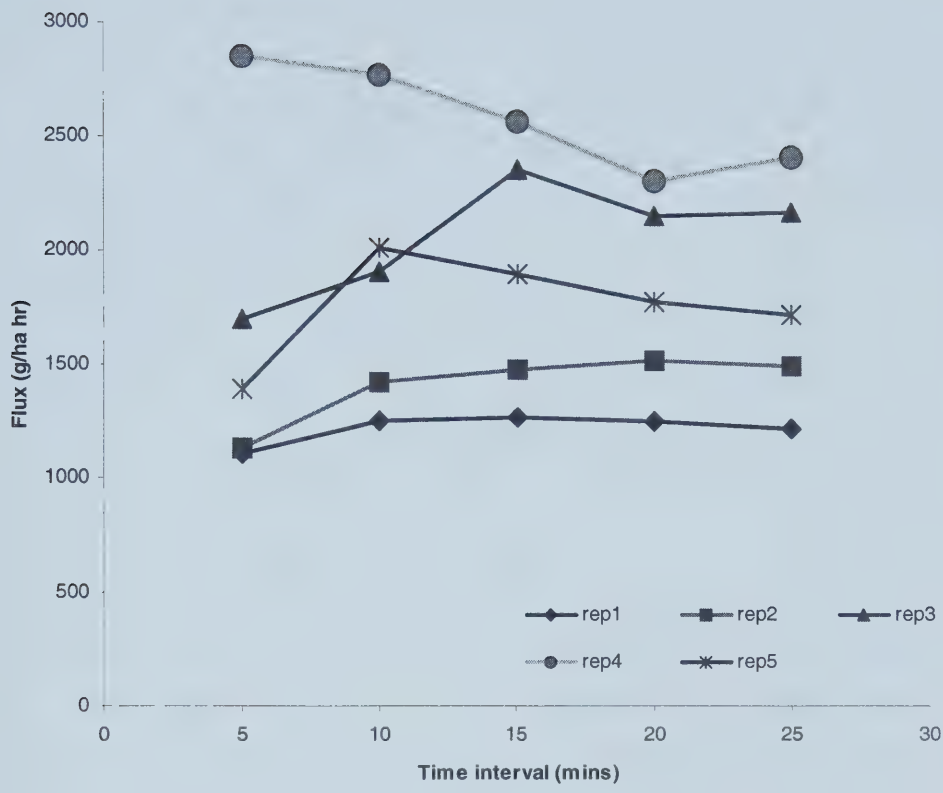


Fig. 2.3. Comparison of fluxes obtained from the H-M model at different sampling times.

2.4.3. Depth of insertion effects on flux estimates from the H-M model

One of the major assumptions in the H-M model is that, at a certain depth close to the upper limits of the production zone, the placement of the soil chamber does not affect the concentration at that depth. However, from the results in Fig 2.4, the depth of insertion appears to significantly influence the flux estimates, implying that the placement of the soil chamber, and the depth of insertion, affected the concentration gradient in the soil profile and subsequently on the flux.

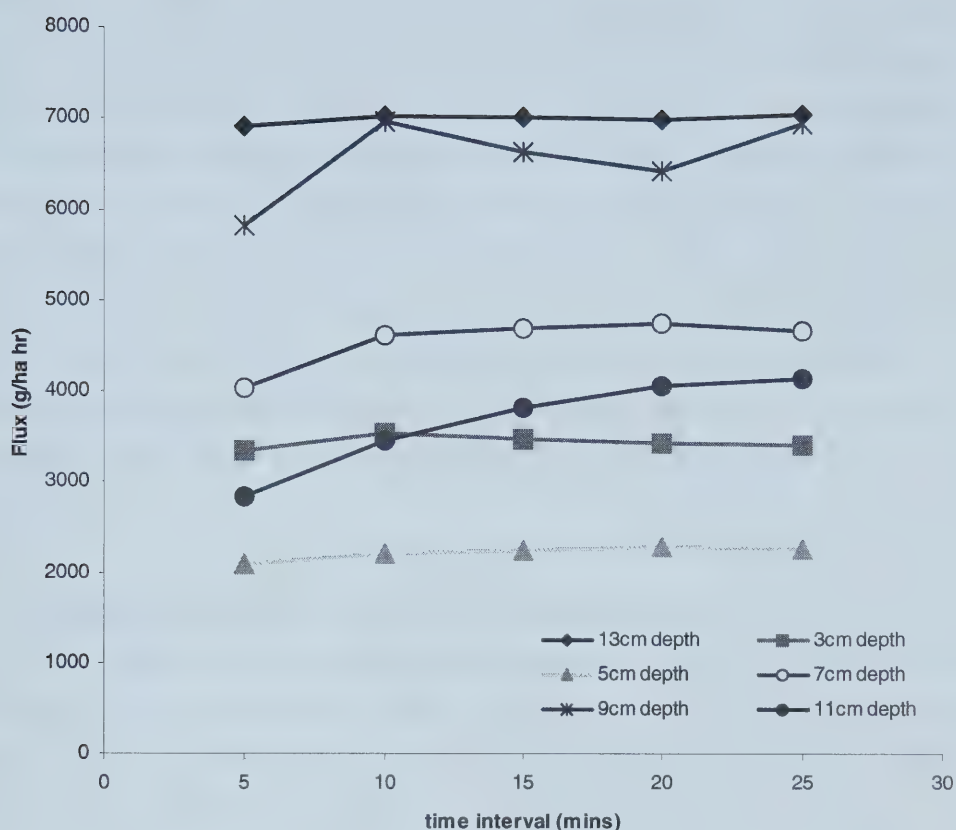


Fig. 2.4. Effect of depth of insertion and sampling interval on flux estimates using the H-M model.

The general trend was a higher flux estimate at greater depths of insertion. However, there are reverses, which can be a result of the spatial variability of flux in the sampling plots as well as sampling time differences. The flux estimates obtained at 13 cm depth of insertion were approximately 3.5 times that obtained at 5 cm depth. This would seem to suggest that the placement of the chamber could be affecting the lateral diffusion of the CO₂ gas in the soil and hence determining how much gas would diffuse into the chamber. The possible flaw with the H-M model is the assumption that a one-dimensional model can explain the exchanges of gases across the soil-atmosphere boundary. This assumption however has not been independently evaluated (Healy et al., 1996). However, Mathias et al. (1978), using a two

dimensional computer simulation of a closed chamber concluded that, under certain conditions the build-up of the gas concentration in the soil cover caused lateral gas movement, decreasing the flux out of the soil into the chamber by as much as 55%. The deeper the chambers are inserted, the greater will be the impediment to the lateral movement of gas into the chamber and to the leakages from the chamber as the gas concentration builds-up. Also, the external effect of wind, which tends to exert a suction force on the gas in the chamber headspace, is reduced. This all leads to a greater degree of gas build-up in the chamber and a lesser loss of gas from the chamber headspace leading to the greater flux estimates. The results show a greater influence of the chamber placement on the flux estimate than the H-M model assumes.

2.4.4. Sampling time effects on linear model flux estimates

The flux estimated from the linear model declined over time for different depths of insertion (Fig 2.5). The decline in the flux is almost linear and is to be expected in the time-dependent distortion that concentration build-up in the chamber causes on the flux (Healy et al., 1996). This trend is a result of the decreasing concentration gradient between the chamber headspace and the soil air due to the concentration build-up and the resultant decline in the rate of diffusion. The results however showed a greater deviation from the decline in flux in the early stages of the experiments by the gradual increase to a peak value before decreasing. This aberration may be explained by the effect of wind action on soil respiration. When the soil is dry as in this case (volumetric water content of 0.17), the wind could have a great effect in flushing the surface layers of the soil of the CO₂ gas leading to a lower concentration gradient immediately after the placement of the soil chamber. A study conducted by Evans et al. (1962) reported that a wind speed of 313 cm/sec at a height of 168 cm led to a decrease of about 10% in the ²²² radon concentration up to a depth of 61cm in the field. The initial high concentration gradient in the soil profile may have caused the higher initial fluxes. However, after chamber placement, concentration gradient reduced and this may have driven the flux down to normal levels.

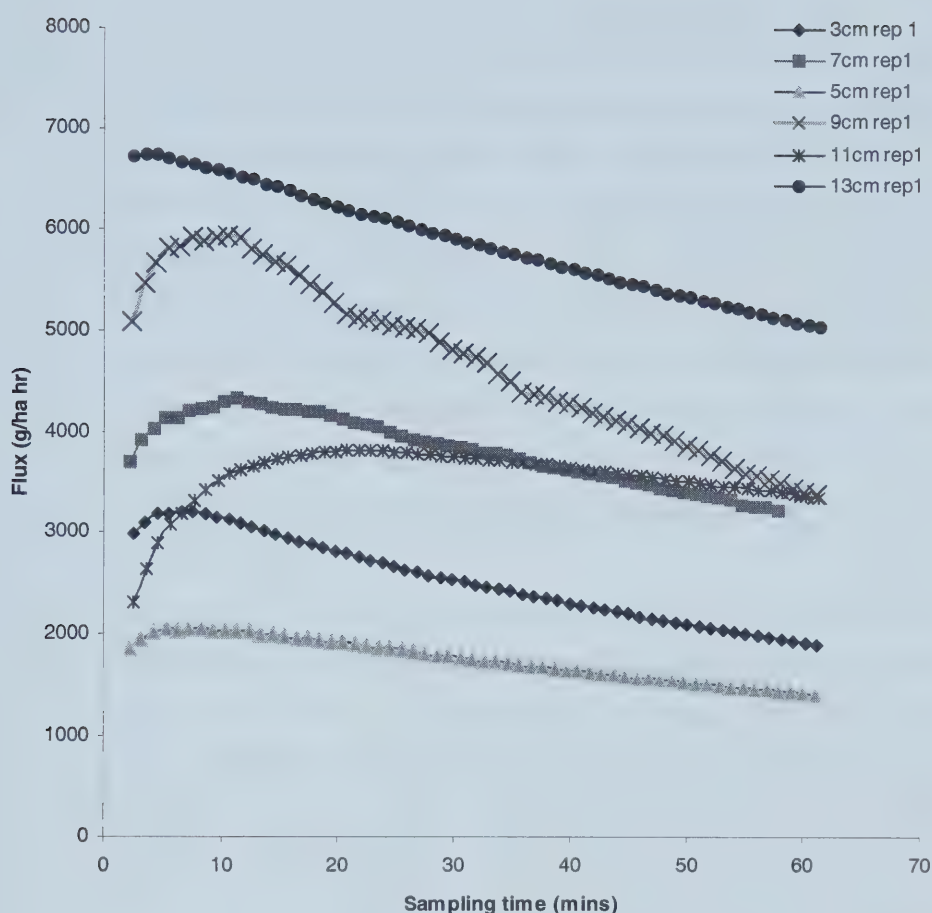


Fig. 2.5. Sampling time effects on linear model flux estimates at different insertion depths

The results also show the wide range of flux estimates with the linear model as the sampling time and depth of insertion changes. The results affirms observation made in the past that the first few minutes after the placement of the chamber could be a period of erratic flux pattern into the chamber headspace. After an initial, short time interval of approximately 15 min, the estimated flux declines continuously with time. This raises serious questions about the use of the linear model. There is no ‘correct’ sampling time at which an unbiased estimate of soil gas flux can be obtained.

2.4.5. Comparison of flux estimates from H-M model and linear model

Fig 2.6 shows the results obtained from comparing flux estimates from the H-M and the linear model. Other researchers have stated that that in most cases, the linear model could produce good estimates of flux without compromising too much on accuracy (Petersen, 1999; Clayton et al., 1994; Ambus and Christensen, 1995). However, our data in Fig 2.6 clearly shows that the linear model, in general, tends to underestimate the flux. This, combined with the fact that the flux estimate of the linear model declines with sampling time, suggests that the underestimation of soil flux by the linear model becomes more serious as sampling time increases. This can be a particularly serious issue for trace gas flux measurements because of the extended sampling times required in order to accumulate sufficient gas in the chamber for measurements.

The linear portion of Fig 2.5 ($t > 15$ min) was extrapolated to $t = 0$ to produce a zero-time flux estimate by the linear model. These are compared to the average flux estimates by the H-M model for $t > 15$ min (Fig 2.4). The results are listed in Table 2.1. Although the ‘extrapolated’ flux from the linear model is still consistently lower than the H-M model estimates, the differences are generally small, or $< 10\%$. These results show that if multiple measurements are made, linear model estimates of flux, extrapolated to $t = 0$, will produce flux values close to those of the H-M model.

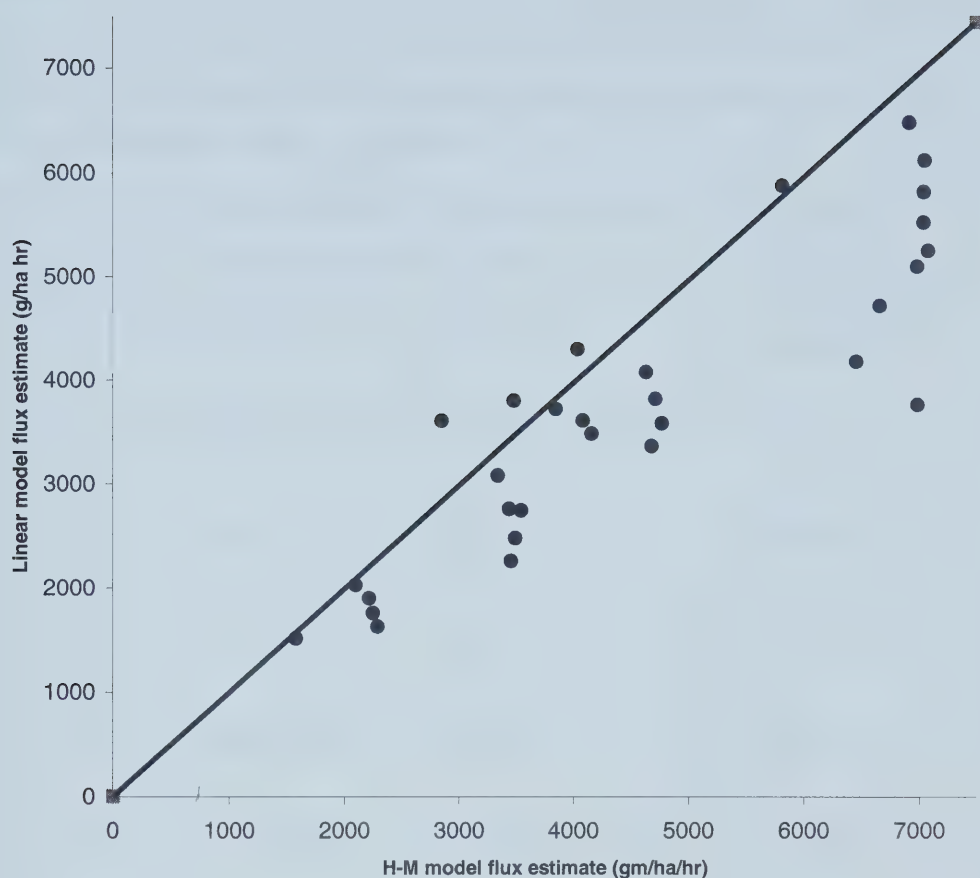


Fig. 2.6. Comparison of flux estimates from the H-M model and the linear model. Flux estimates from the H-M model were plotted against that from the linear model using the same sampling time

Table 2.1. Comparison of linear model extrapolation flux estimate and H-M model flux estimate at sampling time of 15 minutes. The results of the linear model estimates were obtained by extrapolating the trendlines to the linear fluxes to time zero, excluding data before $t = 15$ minutes

Depth of insertion (cm)	Linear model flux estimate (R^2) (gm/ha/hr)	H-M model flux estimate (gm/ha/hr)	% Linear model flux estimate to H-M model flux estimate
13	6844 (0.998)	7267	94.1%
11	3944 (0.77)	4163	94.74%
9	6315 (0.992)	6985	90.4%
7	4600 (0.998)	4678	98.32%
5	2187 (0.998)	2286	95.68%
3	3281 (0.990)	3443	95.3%

At all depths of insertion, the extrapolated linear model produced flux estimates greater than 90% of the flux estimates of the H-M model. This is similar to results obtained in other studies (Clayton et al., 1994; Ambus and Christensen, 1995; Petersen 1999) that have found the linear model as very useful in predicting flux. Given that the depth of insertion produced much higher variations in flux (as high as 3 times the flux at 13 cm relative to that at 5cm), it is logical to conclude that the extrapolation of the linear model will not produce errors greater than the variation caused by the depth of insertion.

2.4.6. The reference chamber headspace concentration function

After the introduction of an instantaneous flux into the chamber headspace a plot of the proportion of CO₂ remaining in the chamber headspace relative to that introduced, P_r , is shown in Fig. 2.7. The integration of this curve produces the reference chamber headspace concentration function, I_0 (Fig. 2.8). The function $I_0(t)$ represents the concentration response of the chamber, if there was an input of a constant flux.

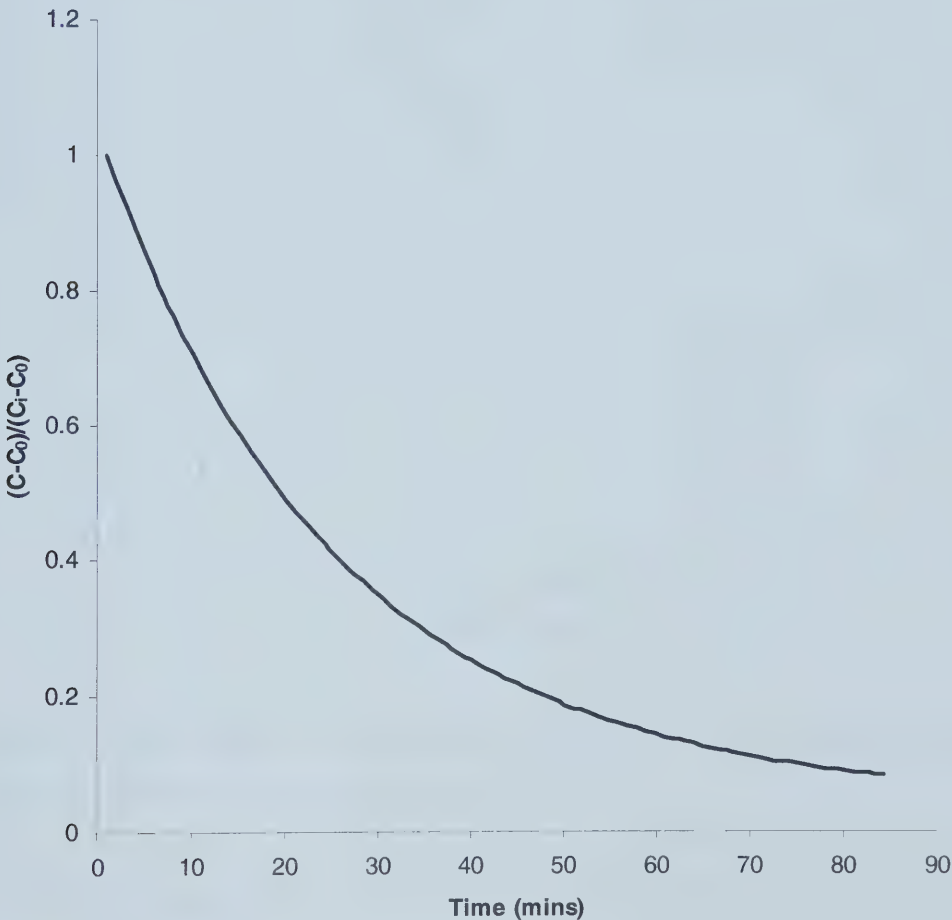


Fig. 2.7. Fraction of CO₂ remaining in the chamber headspace as a function of time in the laboratory diffusion experiment.

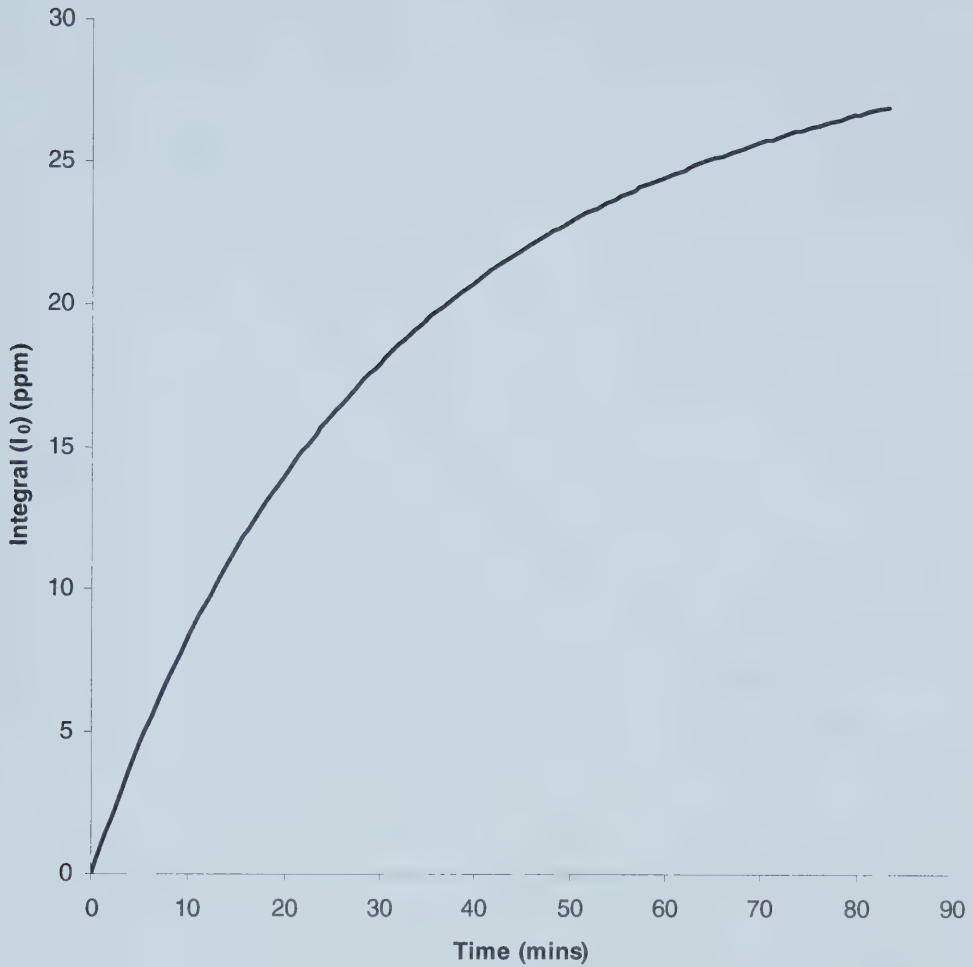


Fig. 2.8. Plot of integral (I_0) vs. time. The curve shows the diffusion response of the chamber at different times in the experiment.

2.4.7. Performance of new model in resolving non-linearity under steady concentration build-up

Fig. 2.9 shows the plots of the non-linearity factor $I_0(t)/2I_0(t/2)$ against t from the laboratory diffusion experiments (see section 2.2.3.). The depth of insertion was 3 cm which is the same as the depth of insertion used for the field experiments.

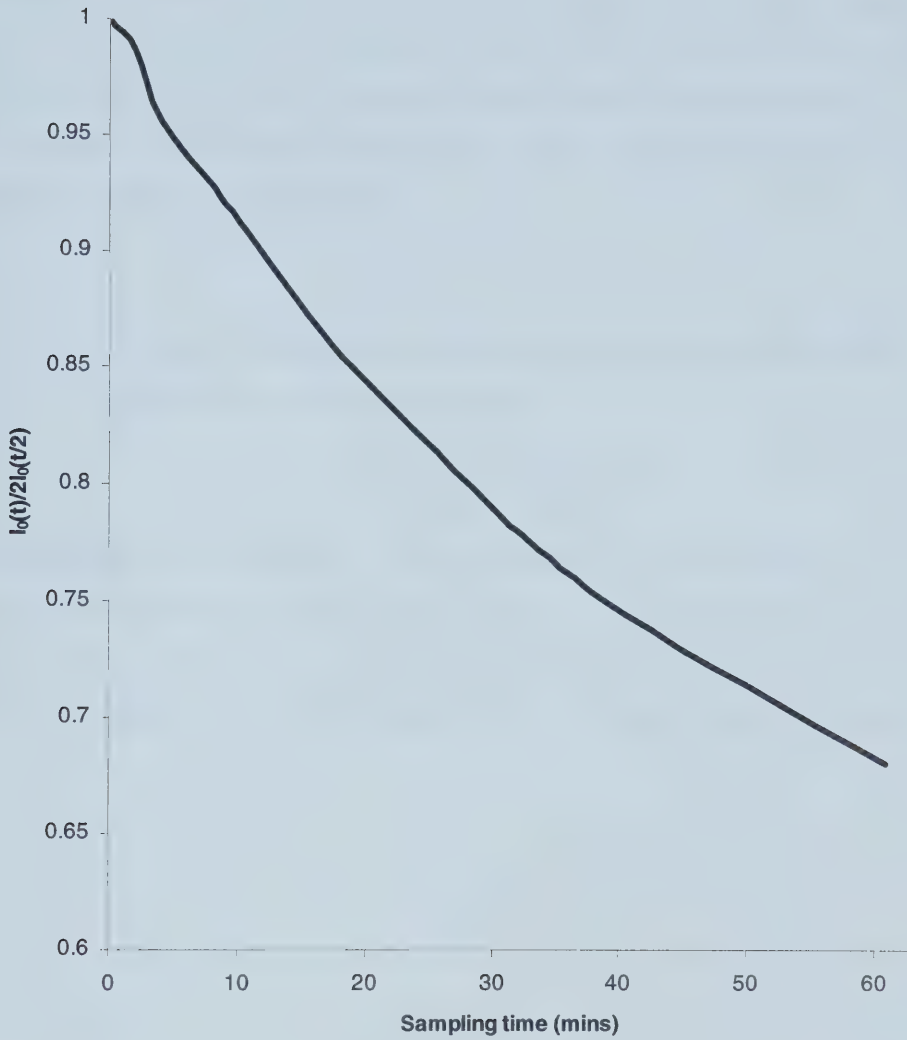


Fig. 2.9. The non-linearity factor $I_0(t)/2I_0(t/2)$ obtained for different sampling times on the reference soil (sand) in a diffusion experiment in the laboratory. This curve is used to determine the scaling factor and the correction factor for the field experiments.

The results from Fig. 2.10 shows that when corrections are made for the non-linearity without factoring in the scaling factor, the estimates obtained deviate from the linear conditions expected such that there seemed to be an over-correction. This occurs when the diffusivity of the field soil is smaller than that of the reference soil. If

the diffusivity of the field soil is greater than the reference soil, an under-correction would occur. This indicates that the appropriate value for the scaling factor must be determined for the field soil so that the correct correction factor can be used.

From data obtained from field experiments using a sampling time of 30 minutes chosen arbitrarily, we obtain value of

$$\frac{C_2 - C_a}{C_1 - C_a} \left(\frac{1}{2} \right) = 0.85$$

From Fig. 2.9, this only corresponds to approximately 20 minutes in the reference soil. This implies that in order for the relationship

$$\left(\frac{I_0(\alpha t_2 / 2)}{2I_0(\alpha t_2 / 2)} \right) = \frac{(C_2 - C_a)}{2(C_1 - C_a)}$$

to be satisfied, a scaling factor, $\alpha = 2/3$ must be used when determining the corrected concentrations. Using this scaling factor, a new plot was obtained which conforms better to the expected concentration build-up in the chamber headspace. The high R^2 of 0.9997 suggest that the result conforms well to the expected linear conditions.

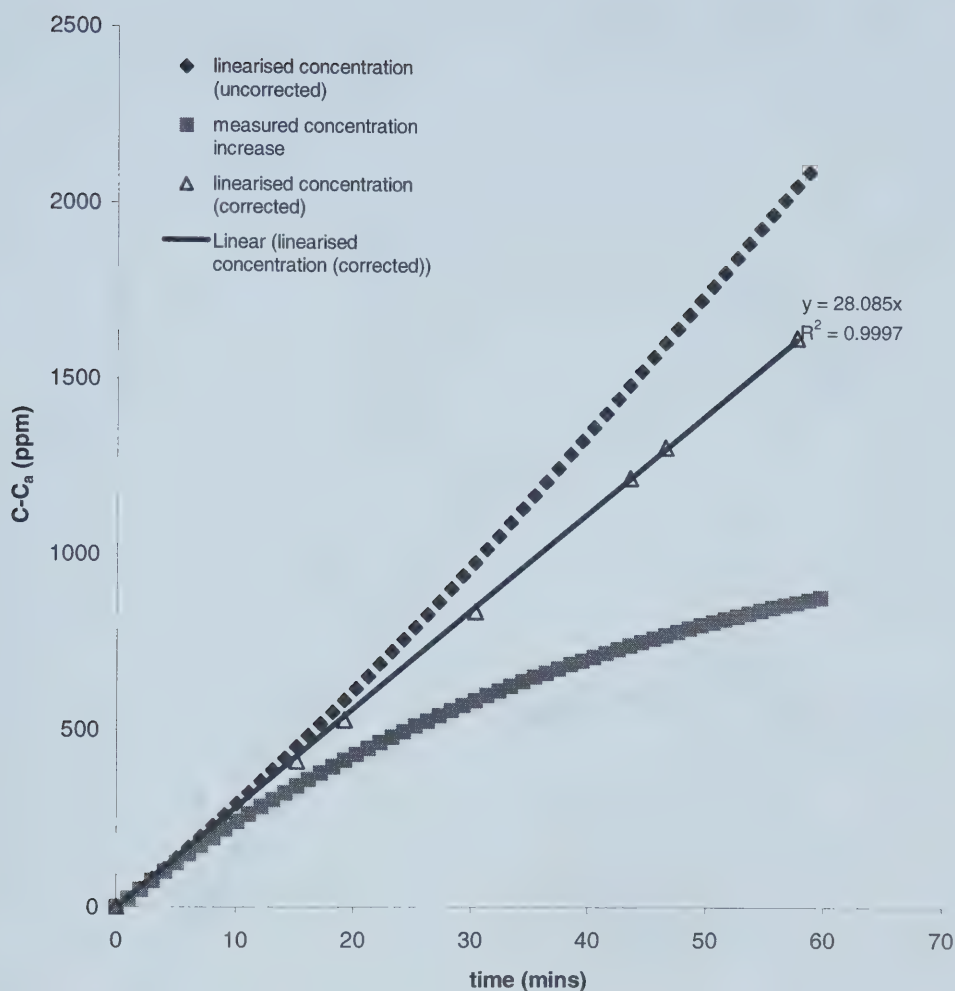


Fig. 2.10. Projections of new model for concentration in the chamber headspace before and after correction for differences in the diffusivities between reference soil (sand) and field soil.

2.4.8. Performance of the new model in predicting flux under fluctuating concentration build-up

Under field conditions many variables exist that affect the concentration build up in the chamber headspace. Atmospheric turbulence has the effect of contributing to mass flow and the apparent diffusivity of the soil (Fukuda, 1955). Fig. 2.11 shows results

obtained when data obtained from the field under atmospheric turbulence was analyzed using the proposed new model.

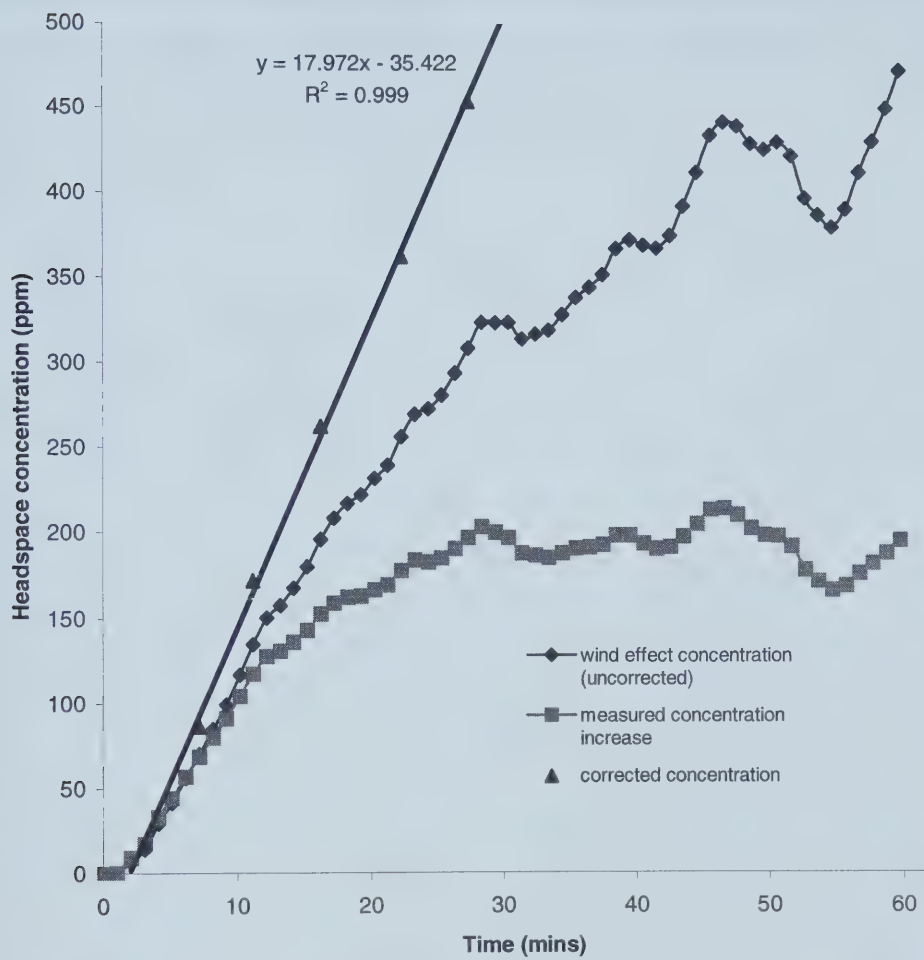


Fig. 2.11. Projections of new model under conditions of fluctuating concentration build-up due to atmospheric turbulence.

Under such conditions, the atmospheric turbulence causes the fluctuation in the concentration build up in the chamber headspace. If, as suggested by the H-M model, only three observations are made, it is likely that the condition $(C_2 - C_1)/(C_1 - C_0) < 1$ will

not be met if C_2 were measured on a downward swing of the concentration. For the new model, if the scaling factor is not used, the corrected concentration is lower than what is expected by the linear relationship. In other words, without using the scaling factor, one obtains an under-correction of the headspace concentration. In this case, using the measured headspace concentration at 30 and 15 min, we obtain

$$\frac{C_2 - C_a}{C_1 - C_a} \cdot \left(\frac{1}{2}\right) = 0.69$$

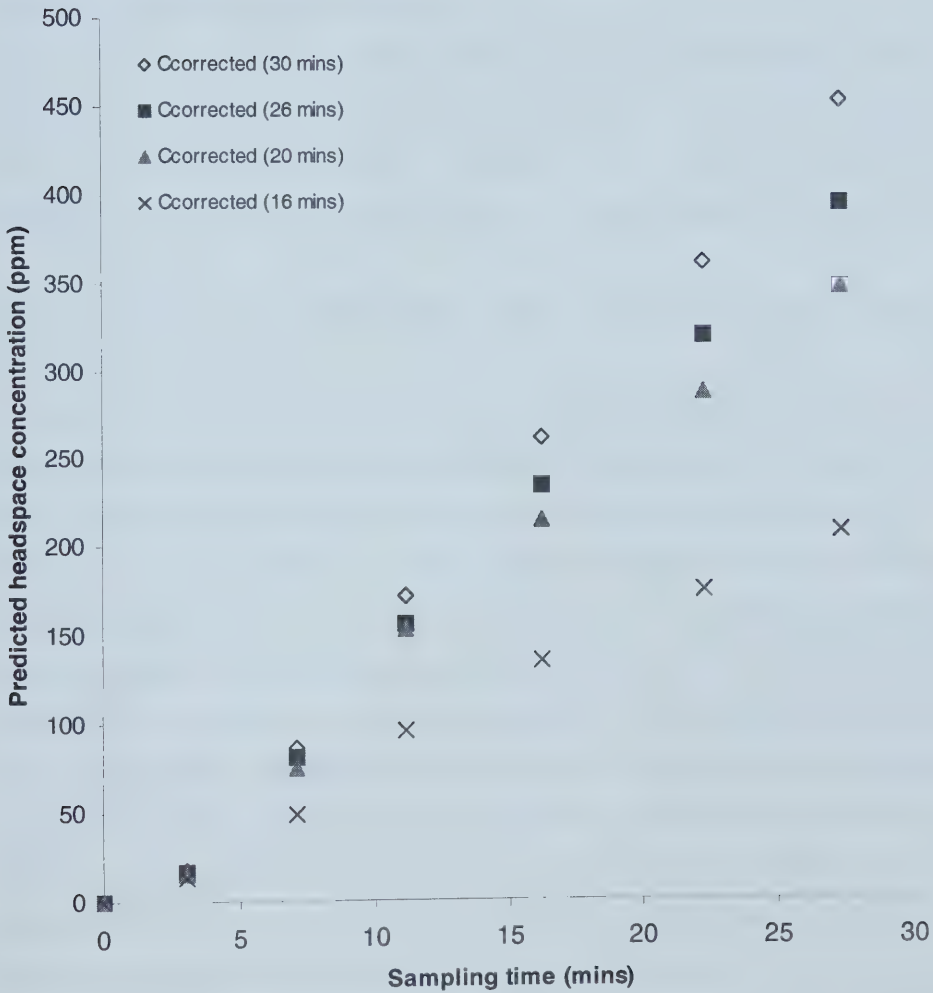


Fig. 2.12. Projected headspace concentration with time by new model based on different sampling times using fluctuating concentration data from Fig. 2.11.

From Fig. 2.9, this corresponds to approximately 60 minutes in the reference soil. Thus, the scaling factor is determined to be $\alpha = 2$. The apparent diffusivity in the soil is twice that in the reference soil. The corrected concentration using this scaling factor is also shown in Figure 2.12, showing nearly perfect linear relationship, as expected. The fact that the scaling factor in this case is >1 , as compared to the data in Fig. 2.10, under calm atmospheric conditions, where the scaling factor was only $2/3$, confirms the assertion that atmospheric turbulence enhances the gas movement in the soil resulting in increased apparent diffusivity.

Fig. 2.12 shows the high sensitivity of the model to the field conditions and the adjustment to the projected headspace concentration accordingly based on these varying conditions as apparent diffusivity changes. This model, if used properly is expected to give a true reflection of the flux as is expected under field conditions.

2.4.9 Comparison of flux estimates from linear models, H-M model and new model

Results from Fig. 2.13 shows comparison of the flux estimates obtained from the H-M, linear and the proposed model at different sampling times (see Appendix C for more results). Generally, the linear model under estimated flux relative to the estimates by the H-M and the new model. The flux estimates from this model also decreased with time due to the impact of non-linearity. In comparison to the H-M model estimates, the linear model underestimated the flux by 21%, 31% and 40% at sampling times of 10, 20 and 30 minutes respectively. These differences are specific to the chamber used in this study and are expected to vary with chamber dimension and size. The proposed model performed well relative to the H-M model but had the added advantage of being very sensitive to changes in the field conditions that affected the diffusivity (see Appendix C). The H-M model in theory and in practice does not account for these changes but the proposed model proves to be able to predict flux under normal conditions and also to adjust the flux accordingly when diffusivity changes. The results of the study show that although the H-M gave

reasonable estimates for flux, the physical basis for the model was not supported by the results.

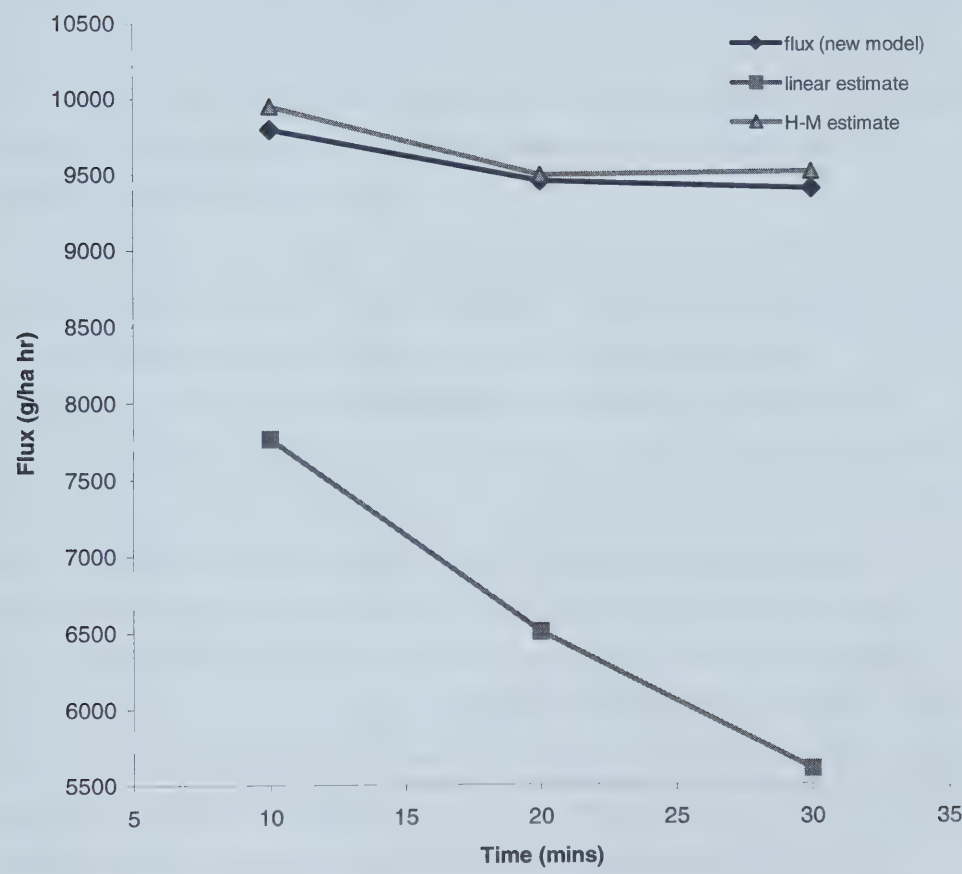


Fig. 2.13. Comparison of flux estimates by linear, H-M and new models using three different sampling times

2.5. CONCLUSIONS

The study revealed clear inconsistencies in the theory on which the H-M model is based. The theory of a constant concentration at the upper limits of production of the

soil was not supported by the data from the study. Flux estimates from both the H-M model and the linear models were greatly influenced by the depth of insertion. The time interval used in the calculation of flux for the H-M model did not greatly affect the flux estimates. However a time interval of 15 minutes and greater is recommended for future studies, in order to reduce the variability in the flux estimates. Generally, the linear model performed poorly against the H-M model and the new model. The estimates obtained from the linear model decreased in accuracy over time. The results of this study suggest therefore that short measurement times are theoretically more appropriate for the linear model, however, this may not be practical because of the following:

- Initial disturbance that results after the placement of the soil chamber
- Trace gases (such as N_2O and CH_4) detection limits for most instruments require long measurement times therefore non-linearity cannot be avoided.

However, comparison of the flux estimates of the linear regression and H-M models showed that the linear model performed quite well in the estimation of flux when extrapolation was done to the time of the placement of the soil chambers. The depth of insertion, from the results of this study, should be of greater concern to researchers in soil gas fluxes than the type of model used in the flux estimation. This is due to the greater variability in the flux estimates by depth of insertion, which could be as high as 5 times greater at greater depths than at shallower depths. This study recommends a depth of insertion of 10cm or greater in contrast to the shallower depths used in most studies in this field. Tests on the proposed model showed it to be accurate in predicting the flux relative to the H-M Model and had the added advantage of being very sensitive to the conditions on the field that alter the diffusivity of the soil. Unlike the H-M model, the new model allowed for corrections to be made based on those changes in the diffusivities of the soil and is therefore a more versatile and dynamic model. In addition, the effect of the depth of insertion may be removed if the reference chamber space concentration function is determined at the same depth of insertion as those used in the laboratory.

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CHAPTER 3. DEPTH OF INSERTION AND WIND EFFECTS ON FLUX ESTIMATES

3.1. INTRODUCTION

The accuracy of the closed chamber methods of soil emission measurements is greatly reliant on the pressure differences between the chamber headspace and the soil air (Denmead et al., 1979). It is reasonable to assume that factors that affect the headspace concentration such as the ambient pressure fluctuations caused by wind action may be a source of influence.

The placement of the soil cover on the surface has the effect of isolating the soil surface from normal atmospheric dynamics especially the pressure fluctuation due to wind movement, which could undermine the accuracy of readings obtained (Ryden et al. 1978). The effect of the placement is not only due to the disturbance of the wind close to the surface of the soil, or the build-up of gas concentrations near the surface of the soil higher than the concentration before the placement, but also as a result of the disturbance of the soil matrix (Jury et al., 1982). This disturbance has the effect of altering the diffusivity of the soil and hence the diffusion of the gas into the chamber headspace. Fukuda (1955) studied the effect of wind gustiness on gaseous and vapour movement in soils and concluded that there was little influence of wind gustiness on the vapour transfer rate. This suggests, therefore, that any disruption of the wind dynamics due to the placement of the chamber should not significantly affect the gaseous flux. However in a critique to Fukuda's conclusions, Hanks and Woodruff (1958) noted that fluctuations of the wind at the soil surface, although they may not cause massive displacement of air from the soil, are likely to speed up the gaseous movement and hence affect the flux. It cannot be disputed that diffusion processes mostly drive gaseous flux from soils. However, they found air turbulence to significantly contribute or influence it and that this will be more pronounced in coarser textured soil and in soils with lower moisture content. Farrel et al. (1966) also noted one other limitation of Fukuda's study was that the treatment ignores the horizontal gradients of the atmospheric pressure at the surface at the surface of the soil.

Pressure fluctuations in the chamber headspace caused either by wind action or by the effect of a mixing fan that some chambers are equipped with, can lead to the phenomenon of mass flow. Mass flow is the influx of CO₂ into the chamber headspace far in excess of the normal diffusion rate due to pressure differential between the chamber headspace and the ambient. Flow rates in the chamber could be ten times normal when very small pressure deficits such as 98 Pa existed (Denmead, 1979). Pressure differentials also arise from the absorbent action of chemicals used in the static chambers and could lead to overestimations in the flux especially under a low emission regime. Scotter and Raats (1969) reported an increase in the dispersion of gas in columns of soil and other porous media as the velocity of the gas flow through the columns was increased, which is the condition most likely prevalent in the top surface layers of the soil.

If the wind dynamics does indeed have an effect on the build-up of gas in the chamber headspace, then it is logical to assume that the depth of insertion of the chamber into the soil should be an important factor in this. Healy et al. (1996) observed that the chamber dimensions as well as the depth of insertion affected flux. The deeper the chambers were inserted in the soil, the greater was the estimated flux. This is because radial diffusion of gases out of the chamber headspace was reduced or eliminated as the chambers were inserted deeper in the soil. Various depths of insertion have been used in the past by different researchers in this field ranging from 0.5 cm (Nay and Bormann, 2000) to 10 cm (Bajracharya et al., 2000). Unfortunately, not much work has been done in this area to quantify the effect of depth of insertion on the flux. The result is that most researchers working with gas chambers do not factor in the depth of insertion in any estimates for flux that are obtained. In this study, the effects of the wind as well as the depth of insertion on the headspace concentration build up as well as the flux estimates.

3.2. MATERIALS AND METHODS

3.2.1. Laboratory experiments

A LI-6400 portable photosynthesis system (LI-COR Inc., Lincoln, Nebraska) was fitted with a cylindrical CO₂ chamber (See Appendix A). The soil surface area sampled was 71.6 cm². Diffusion experiments (Fig. 3.2) were conducted on a sand box (40 cm deep, 50 cm wide) filled with clean sand (bulk density 1.77 Mg/m³). Four soil collars were utilized in the soil collar experiments. The soil collars were constructed from fiberglass and had an internal diameter of 10 cm to allow the chamber to fit in and an external width, w of 1.5 cm, 3 cm, 6 cm and 9 cm respectively (Fig. 3.1). Diffusion experiments were all conducted after the injection of about 2700-2900 ppm of CO₂ into the chamber and then monitoring of the concentration in the chamber was done over a period of 1-2 hours by the IRGA. The data logging was done at 1-minute intervals.

3.2.1.1. Effect of collar on diffusion

The soil chamber was fitted with 3 different sizes of soil collars (1.5 cm, 3 cm and 6 cm). About 3700 ppm, CO₂ was injected into the chamber and the concentration change in the chamber headspace was monitored over time with the IRGA. The first set of experiments was conducted at a depth of insertion of 3 cm. The second set of experiments was conducted on the soil surface using three different collar sizes (1.5, 3 and 6 cm).

3.2.1.2. Effect of depth of insertion on the flux

Brass cylinders of different heights and diameter 10 cm fitted unto the IRGA soil chamber such that a fixed headspace volume was obtained whilst the depth of insertion varied at 3 cm, 5 cm, 7 cm, 9 cm, 11 cm and 13 cm. The concentration of CO₂ gas in the soil was monitored for an hour, using the IRGA, for each experiment.

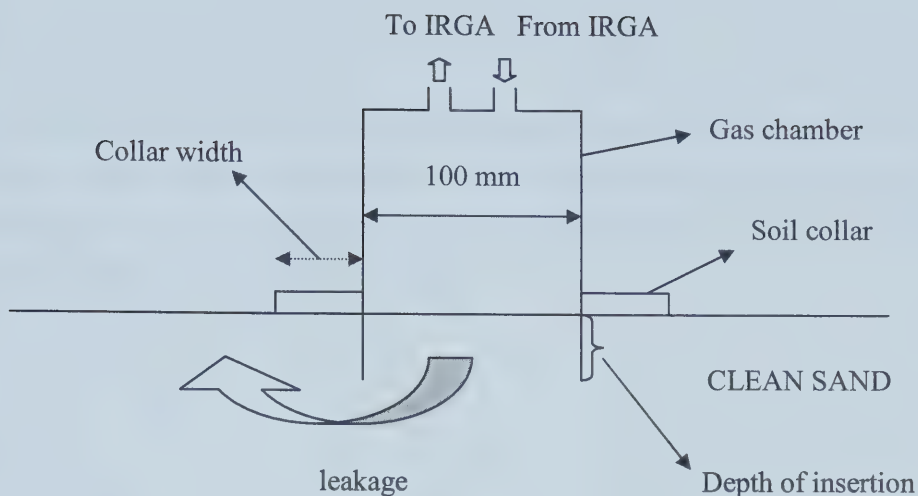


Fig. 3.1. Schematic diagram of diffusion experiment set-up on a sand-box. Concentration in the chamber after the injection of the CO_2 was monitored using the LI-6400 IRGA.

3.2.2. Field experiments

Field experiments were conducted, using the same apparatus, at the University of Alberta Research station at Ellerslie in the summer and fall months of 2002 (see Appendix B for site description).

3.2.2.1. Effect of wind and collar size on flux

The effect of the wind fluctuation on the flux of CO_2 into the soil chamber and how the size of the soil collars affected this was investigated. Three different collar sizes were used (1.5 cm, 6 cm and 9 cm) and the depth of insertion was 3 cm in all experiments. The experiments were conducted on a windy day with average wind speed of 22.2 km/hour. Another experiment was conducted on the same day with the 1.5 cm collar with the soil chamber covered with a box to investigate the effectiveness of this type of covering in reducing the effect of wind on flux.

3.3. RESULTS AND DISCUSSION

3.3.1. Factors influencing the diffusion of CO₂ gas from chamber headspace

Figs. 3.2. shows results obtained from the laboratory diffusion experiments using different collar sizes to investigate the extent of leakage of the CO₂ gas from the chamber headspace when flux is eliminated.

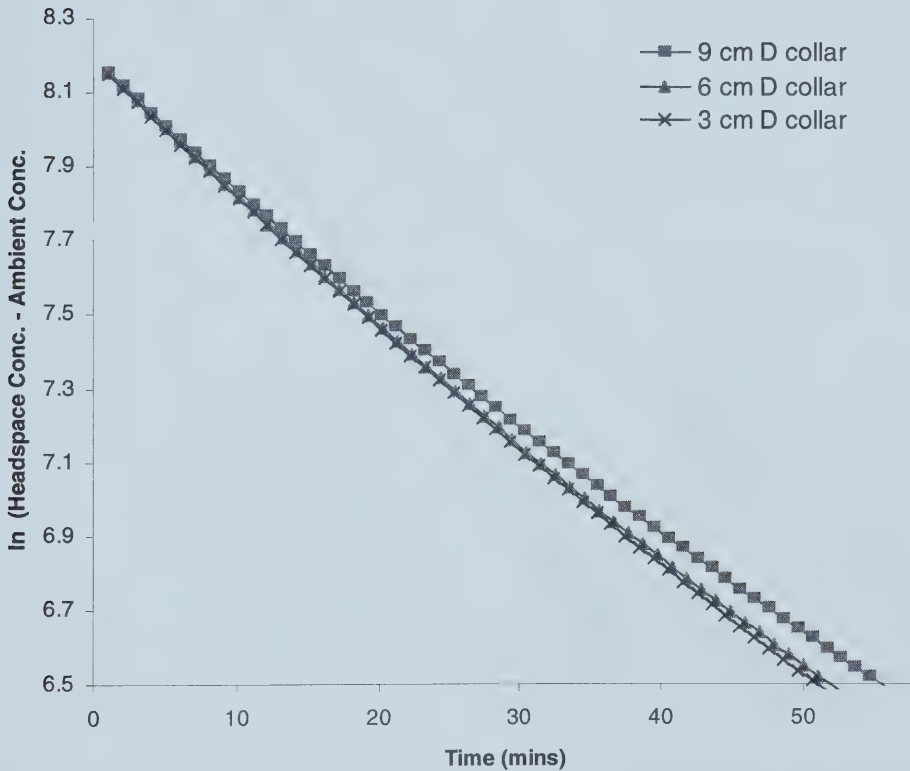


Fig. 3.2. Effect of collar on diffusion of CO₂ at 3 cm depth of insertion. The graph shows the natural logarithm of the concentration in the chamber headspace minus ambient CO₂ concentration plotted against time.

The results show that at the 3 cm depth of insertion, the diffusion of the gas from the chamber was affected by the size of the collar such that the concentration of CO₂

in the chamber declined faster with a decrease in the size of the collar. This could imply that the collars were inhibiting the leakage of gas around the chamber edges.

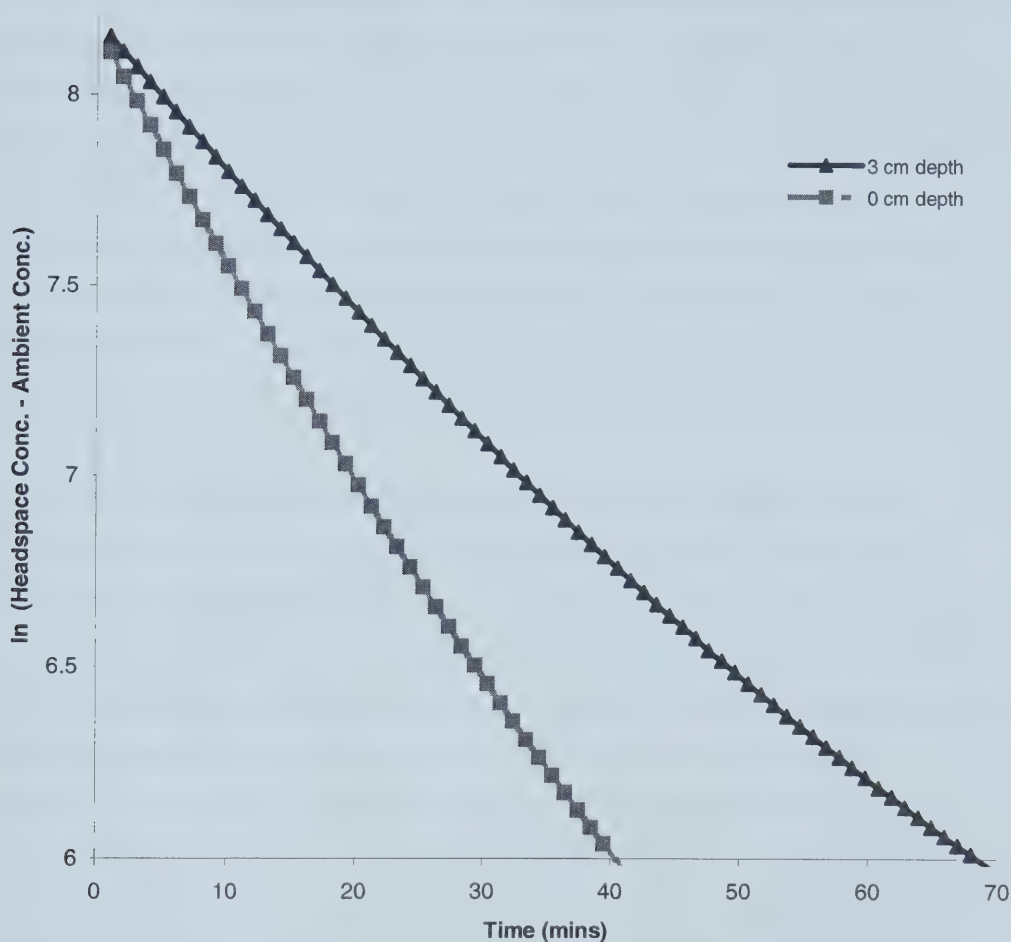


Fig. 3.3. Diffusion of CO₂ at two different depths of insertion; 3 cm and surface. The natural logarithm of the difference between the chamber headspace concentration and the ambient is plotted against time

One may conclude from these results that the use of collars up to 6 cm, does not significantly influence the reference chamber concentration when the depth of insertion is at 3 cm. Thus, in field experiments, small collars may be used to provide

better seal between the soil and the chamber without influencing the gas diffusion process.

Fig. 3.3. shows the plots of the diffusion of the CO₂ gas at two different depths of insertion (3 cm and surface), without collar. The diffusion rate of the gases from the chamber was much higher at the zero depth of insertion than at 3 cm depth. This faster rate of decline could be due to the added effect of lateral or radial movement of gas in the soil (Healy et al., 1996). Leakage also occurs at a greater rate at the surface than at 3 cm depth, when the chamber wall acts as a barrier to these processes.

Since the reference chamber headspace concentration function, the scaling factor and the correction factors are all obtained from these measurements, it is apparent that the depth of insertion, especially at shallow depths, will greatly influence the diffusion process in soils and the resulting flux determination (Refer to chapter 2).

3.3.2. Effect of depth of insertion on head space gas concentration buildup

The results in Fig 3.4 and Fig 3.5 show the concentration of CO₂ in the chamber headspace as monitored with the IRGA. In both situations, the chamber concentration build-up was generally higher at deeper depths of insertion. Also, the non-linearity is much more pronounced at shallower depths of insertion. At the 13 cm depth, the final headspace concentration was approximately 2.25 times that at 3 cm depth of insertion. This could be explained by the fact that at greater depths of insertion, the reverse diffusion of gas from the chamber head space to the outside atmosphere is much slower. Since most models only account for flux due to concentration gradient between the chamber headspace and the soil air, and not for leakages, these results imply deeper depths of insertion will give a more accurate estimation of the true flux. Ryden et al. (1978), reported results similar to that obtained in this study, and recommended a depth of insertion of 10 cm in order to reduce the effects on flux of the pressure differential between the chamber air and the atmosphere. A higher pressure differential could have the effect of inducing diversion of CO₂ produced in the lower layers of the soil around the edges and out of the chamber instead of diffusing into the chamber.

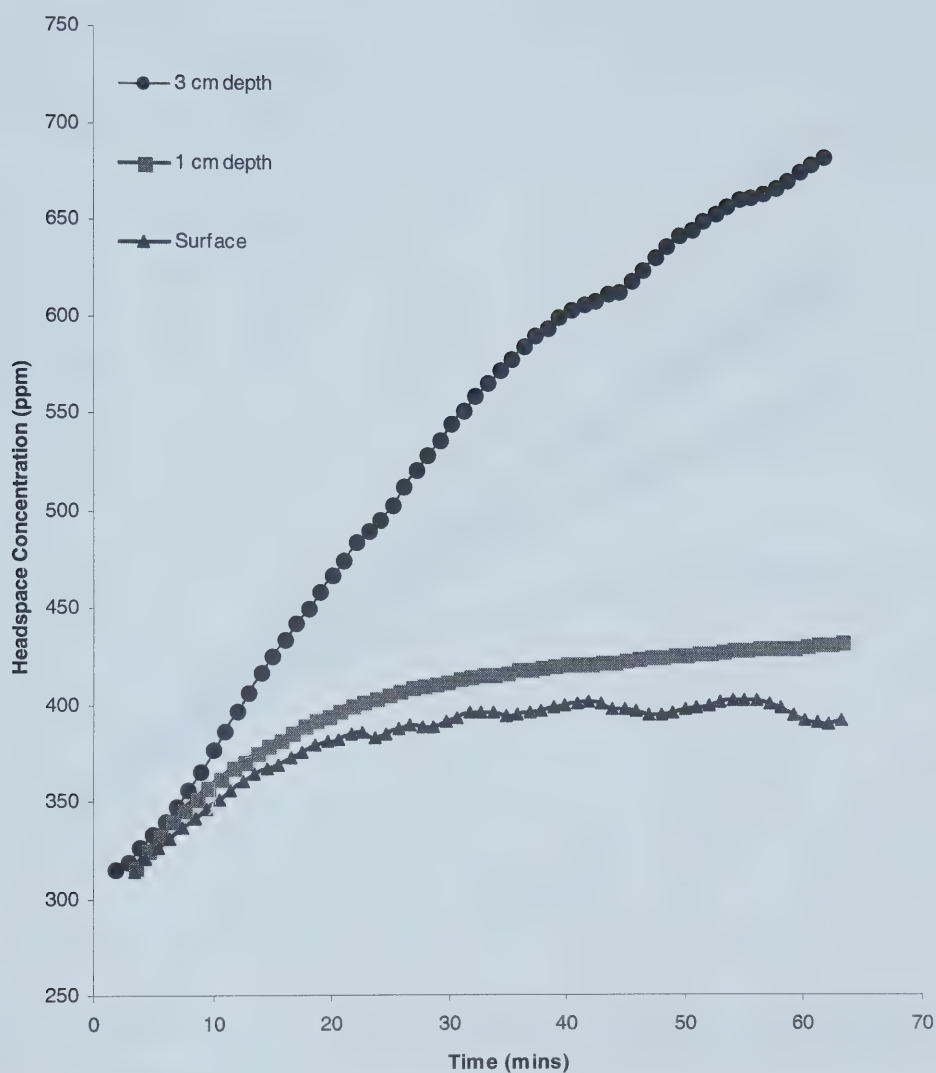


Fig. 3.4. Effect of depth of insertion of chamber on headspace concentration under variable headspace volume.

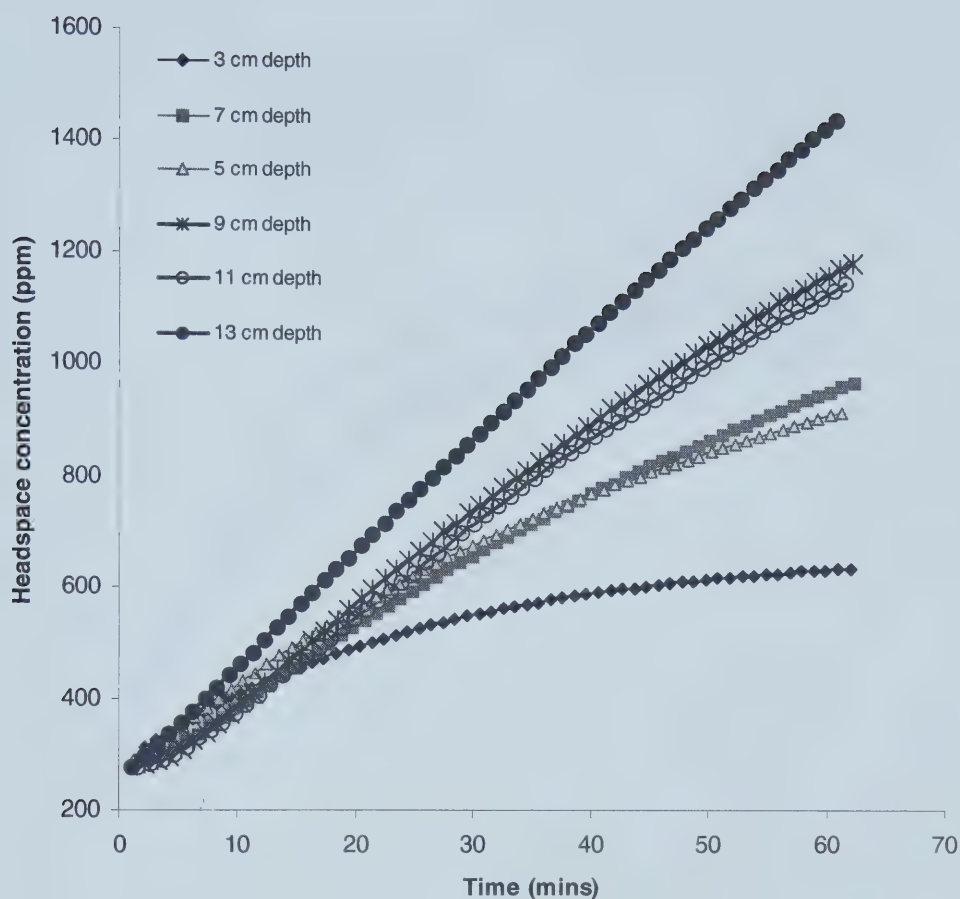


Fig. 3.5. Effect of depth of insertion of chamber on headspace concentration under fixed headspace volume.

3.3.3. Effect of wind and atmospheric turbulence on flux

The results in Fig 3.6. show how strong wind influences the chamber headspace concentration in the closed chamber method. In the exposed chamber with no collars, there was a characteristic fluctuation in the concentration of gas in the chamber headspace.

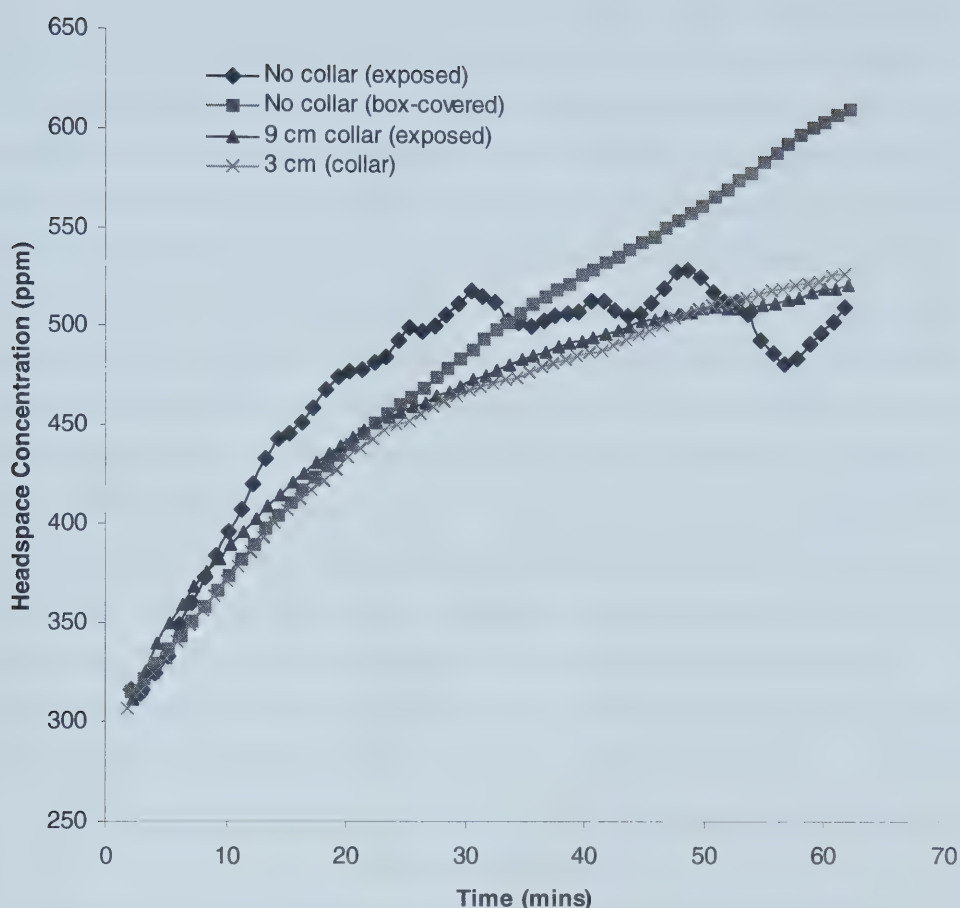


Fig. 3.6. Effect of air turbulence on flux at 3 cm insertion depth. Chamber headspace concentration was monitored on a windy day (average wind speed 22.2km/hr).

The flux obtained from such measurements is expected to have higher errors, even with the use of correct correction factors for the new model (refer to chapter 2). For the H-M model, when only three measurements are made, it is likely that the condition $(C_1 - C_0)/(C_2 - C_1) > 1$ will not be satisfied and therefore the model can not be used to calculate flux. The use of a linear model, on the other hand, even with the extrapolation of flux to $t = 0$, is likely to produce high variability of results. Studies conducted by Kimball and Lemon (1971) support this observation that wind creates pressure fluctuations in the chamber and could lead to mass flow or to a

decline in concentration due to suction. Scotter and Raats (1969) reported a similar observation that air turbulence does indeed affect soil gas exchange, particularly at shallow depths in porous soils. This is likely to affect dry coarse-textured soils. In the first half of the experiment, the concentration build-up in the uncovered chamber shows evidence of mass flow of CO₂ gas into the chamber. Kanemasu et al. (1974) reported in their study on dynamic soil chambers that pressure differential between the chamber air and the atmosphere could lead to mass flow of gas through the soil atmosphere into the enclosed air space. This could lead to a sampling of an unknown volume of soil (Ryden et al., 1978). In contrast, the box covered soil chamber seemed to have reduced the wind effect, thereby yielding a more consistent and smoother concentration build-up. Comparing the two curves for the no-collar, exposed chamber and the no-collar, box covered, indicates some extent of mass flow in the chamber in the first half of the experiment and an unstable peak in the second half of the experiment. The soil collars reduced the effect of the wind by eliminating the fluctuation in the CO₂ gas concentration build-up. However, the concentration build-up was higher in the box-covered chamber than with the soil collars.

3.4. CONCLUSIONS

The study shows that leakage and lateral movement of gases could greatly influence the concentration build up in the chamber headspace and undermine the flux estimates from the closed chamber method if these factors are not accounted for. Although diffusion was found to be the major mechanism driving flux, air turbulence also was found to drive and to suppress flux as observed in the study by Kimball and Lemon (1971). Covering of the chamber by a box was found to increase concentration build-up in the chamber headspace and reduce the effect of wind. Increasing the depth of insertion and the use of collars also reduce the effect of wind. Since the linear model and the H-M model do not take these factors into account, the flux estimates obtained from these models will vary when the experimental conditions change. However, with the use of the new model, these factors can be taken into account by using the reference chamber headspace concentration factor

that is determined under the exact experimental conditions (e.g., collar, cover, depth of insertion) as those used in the field and produce correct flux values.

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CHAPTER 4. EFFECTIVENESS OF GAS TRAPS USED IN THE STATIC SOIL CHAMBER METHOD

4.1. INTRODUCTION

Of the methods available for measuring gas exchange across the soil-atmosphere boundary, static chambers are the most widely used (Healy et al., 1996, Schutz and Seiler, 1989). This is most likely due to the low cost of the method and the ease of use. The static chamber method employs an absorbent chemical such NaOH or BaOH placed under an inverted chamber (Kanemasu et al., 1974). Witkamp (1969) found that flux obtained from the static chamber method was 20% less than that from the dynamic closed chamber method, which utilizes a gas analyzer or a series of samples for gas chromatography analyses instead of the gas traps to determine the CO₂ concentration. There are modifications to the static chamber method such as the method utilized by Otten et al. (2000) in their study of the CO₂ emissions from soils after deformation. The gas trap mechanism used in that study consisted of 0.05M KOH with the electrical resistance of the solution monitored as a function of the amount of CO₂ converted to CO₃²⁻. In terms of molarity of the gas traps, differences exist from study to study. While Otten et al. (2000) used a 0.05M KOH solution; Franzluebbers et al. (2000) employed canning jars containing a vial with 10ml of 1M NaOH to absorb the CO₂. Franzluebbers et al. (2002) 10 ml of 1M KOH solution was hung in the soil chamber by a wire. Their study employed the use of a blank solution of alkaline not exposed to the soil during the measurement process to adjust the measured CO₂ concentration for CO₂ absorbed from the atmosphere during the measurement period and also during titration. Other variations have been the use of soda lime pellets as absorbents (Nay et al., 1994).

The issue of the accuracy of static chambers has been discussed in a few studies. Although static chamber methods are not very accurate, proponents of the method argue for its relevance by the fact that they are more suited for measuring fluxes in areas of high spatial variability (Ambus and Christensen, 1995) or when relationships between gas fluxes and environmental factors are being investigated (Petersen, 1999). In a critique of the dynamic chamber method as opposed to the static chamber

method, Franzluebbers et al. (2002) reported that the dynamic method often yielded unrealistically high fluxes. In one experiment, the fluxes obtained from the dynamic method suggested a 100% decomposition of maize residue in only 11 days whilst the static chamber method suggested a 30% decomposition rate over 4 months, which was more realistic. Another critique of the dynamic chamber method in favor of the static method was offered in the study by Ham et al. (1995). They found that the rate of soil respiration estimated with a small dynamic chamber method was nearly equivalent to that of the whole ecosystem respiration under a large dynamic chamber, suggesting that the above-ground plant dark respiration of live biomass would have been negligible. Raich et al. (1990) observed no difference in respiration between two chamber methods with different exposure times to alkali (24 hours and 30 minutes) and concluded that this indicated that the gas fluxes were not increased by the process of CO₂ absorption by the alkali. Other studies however, have questioned the reliability of the static chamber method. Nay et al. (1994) used Fick's law to simulate the diffusion of CO₂ through a porous medium to compare the flux estimates obtained from a static and a dynamic chamber set up on the porous media. Although both methods showed a slight deviation from the Fick's law ideal, that of the static chamber was more diverse. Under low flux, the static chamber overestimated flux by 25% whilst under high flux; it under-estimate flux by 57%. This result supports observations made from other studies that have found that the static chambers tend to induce mass flow in soils under low emissions of CO₂, which could lead to an over-estimation of flux. However, under high emissions, the gas traps may not perform very efficiently in absorbing the gas in a timely manner.

The objective of this study was to assess the absorption efficiency of 1M NaOH under various conditions.

4.2. MATERIALS AND METHODS

4.2.1. Laboratory experiments

A series of experiments were conducted in the laboratory to investigate the absorption efficiency of 1M NaOH under various conditions. The first of experiments

was to identify the role that the NaOH container size (surface area) plays in the absorption of CO₂. Two different container sizes were used (3 cm and 5 cm diameter) and 5 ml of the alkaline was used in both experiments, for both containers. The set-up of for this experiment involved the soil chamber being sealed onto a table by using sealant grease with alkaline placed in the chamber. CO₂ gas was then injected into the chamber. The CO₂ concentration in the chamber headspace was monitored using a LI-COR LI-6400 Infrared gas analyzer (LI-COR Inc., Lincoln, Nebraska). The second set of laboratory experiments were conducted on a sandbox filled with clean sand with a bulk density of 1.77 Mg/m³. In these experiments the interaction between diffusion of CO₂ out of the chamber and absorption by the NaOH of was investigated. 5ml of a 1M NaOH was used in these experiments. The concentration of the injected CO₂ was monitored using the LICOR LI-6400 infrared gas analyzer.

4.2.2. Theory of NaOH absorption of CO₂

The assumption is that the absorption of the CO₂ from the chamber headspace by the NaOH follows a first order relationship that is dependent solely on the difference between the headspace concentration of CO₂. The rate of change of concentration in the chamber headspace relative to the ambient

$$dC_H / dt = -C_H k \quad [1]$$

where C_H is the concentration of the CO₂ in the chamber headspace and t is the time elapsed after the placement of the chamber

From the relationship above,

$$\frac{dC_H}{C_H} = -k dt \quad [2]$$

Integrating,

$$\int_{C_0}^C \frac{dC_H}{C_H} = \int_0^t -k dt \quad [3]$$

$$\ln C_H = -kt + \ln C_0 \quad [4]$$

Where C_0 is the headspace concentration at time zero. This is in the form of an equation of a straight line:

$$y = mx + c \quad [5]$$

From the relationship above, a plot of $\ln C_H$ against t should yield a straight line with an intercept of $\ln C_0$.

4.2.3. Field experiments

All field experiments were conducted at the University of Alberta Research Station at Ellerslie (see Appendix B for site description). The performance of the chemical traps using different container sizes (3 cm and 5 cm diameter) under both low and high fluxes was investigated in these field experiments. The same volume of gas trap (5 ml of 0.5 M NaOH) was used in the field experiments as in the laboratory experiments. The depth of insertion was maintained at 3 cm for all experiments. The CO₂ gas concentration in the chamber headspace was monitored using the LICOR LI-6400 IRGA.

4.3. RESULTS AND DISCUSSIONS

4.3.1. Effect of container size on NaOH absorption efficiency of CO₂

There was an increase in the absorption rate of the CO₂ as the container size increased (Fig 4.1). The injected gas was absorbed faster by the alkaline in the larger container. The increased surface area of the gas trap could have led to more area for the reaction to take place and hence more CO₂ gas absorbed. However, the time lag for the NaOH to absorb the CO₂ gas supports the critique of the static chamber as not being very efficient in absorbing flux in a timely manner, thereby introducing bias (Freijer and Bouten, 1991, Nakadai et al., 1993). Using the 5 cm diameter container, it took 30 minutes to absorb the injected CO₂ gas whilst for the 3 cm diameter container it took approximately 60 minutes. The issue of time lag in the absorption of the CO₂ gas by the alkali could have lead to a considerable amount of underestimation of flux as observed in other studies (Bajracharya et al., 2000).

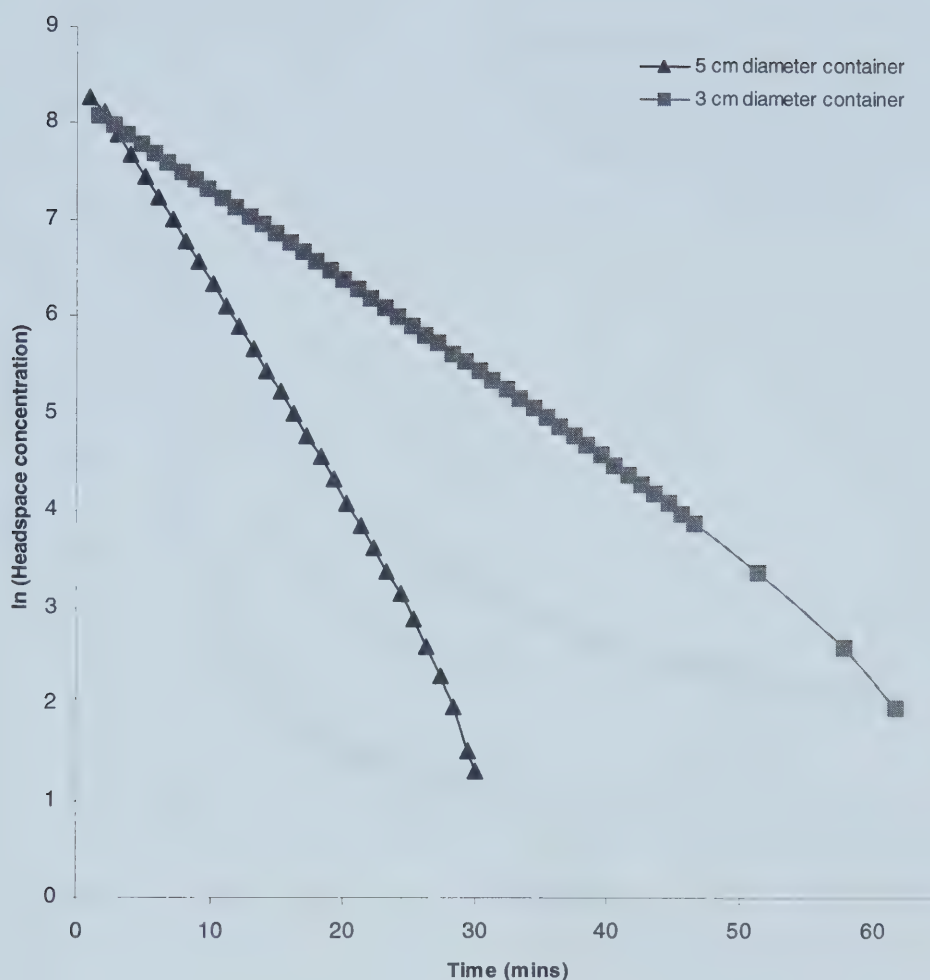


Fig. 4.1. Effect of container size on 1M NaOH absorption of CO₂. The graph shows a plot of the natural log of the headspace concentration against time for two experiments run using two different container sizes (3 cm and 5 cm diameter)

4.3.2. Interaction between CO₂ diffusion and absorption

The results represented in Fig 4.2 show the pattern of CO₂ absorption by the NaOH when chamber was placed on the soil or sealed on a table. For the experiments not involving NaOH, there was a faster decline in the concentration in the chamber placed on the surface than when inserted at a 3 cm depth.

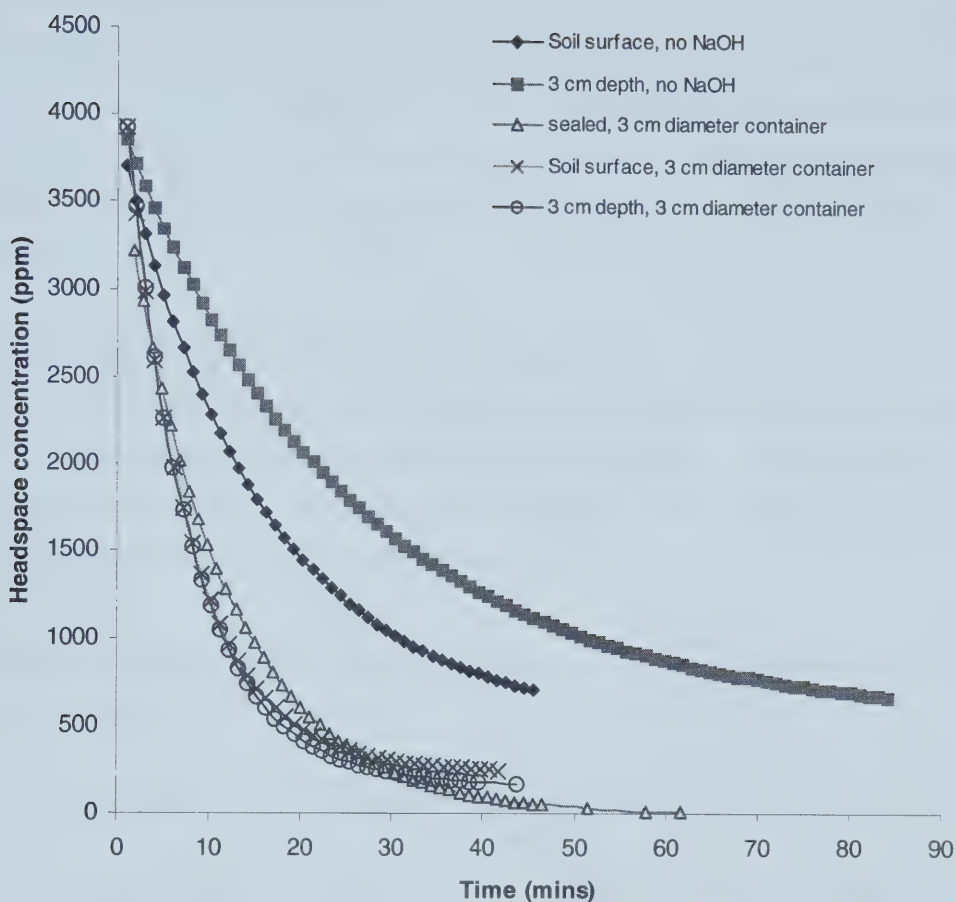


Fig. 4.2. Interaction between CO₂ diffusion and absorption. The graph compares diffusion and absorption patterns in the soil with the absorption of CO₂ from the chamber headspace in the table-sealed chamber

This could be due to processes other than diffusion coming to play such as leakage of the gas around the edges of the chamber. In the experiments that involved NaOH however, in the initial stages, there was a faster rate of decline in the CO₂ concentration in the on-soil experiments than in the on-table experiments. That was most likely due to the combined effect of diffusion and absorption. However around 30 minutes into the experiments, when the concentration in the chamber headspace fell below the ambient levels (330 ppm), the trend reversed with the concentration

stabilizing just around the ambient levels. This effect was more pronounced at a depth of insertion of 0 cm. The explanation for this trend lies in the phenomenon of diffusion. As has been reported in other literature, the gas traps could actually induce diffusion of gas outside the enclosure when the concentration falls below the ambient levels (Denmead, 1979). This could lead to an overestimation of flux under field conditions.

4.3.3. NaOH absorption efficiency and container size

The results from Table 4.1, show that comparatively, diffusion could account for a large proportion of the loss of gas from the chamber headspace. This could lead to underestimation in the flux since the opportunity always exists for the loss of the CO₂ from the chamber headspace through diffusion alone.

Table 4.1. Comparison of first order rate constants of CO₂ absorption by 1M NaOH and by diffusion

Condition	NaOH present	Size of NaOH container	K	R ²
Sealed on table	Yes	5cm	-0.232	0.9958
Sealed on table	Yes	3cm	-0.0953	0.9969
On soil surface	No	-	-0.0523	0.9921
3cm depth of insertion	No	-	-0.0301	0.9921

Using a 5 cm diameter container for the NaOH gave a *k* value almost 2.5 times that when the 3 cm diameter container was used. This was probably due to the larger area of the gas trap coming into contact with a greater volume of the CO₂ gas. The surface area of the 5 cm diameter container is 2.8 times that of the 3 cm container. These results are consistent with the assumption that the rate of gas absorption in the chamber is proportional to the surface area of the gas trap. Figs. 4.3 and 4.4 show the dynamics in the concentration of CO₂ in the chamber headspace with and without sodium hydroxide, under conditions of low flux and high flux respectively.

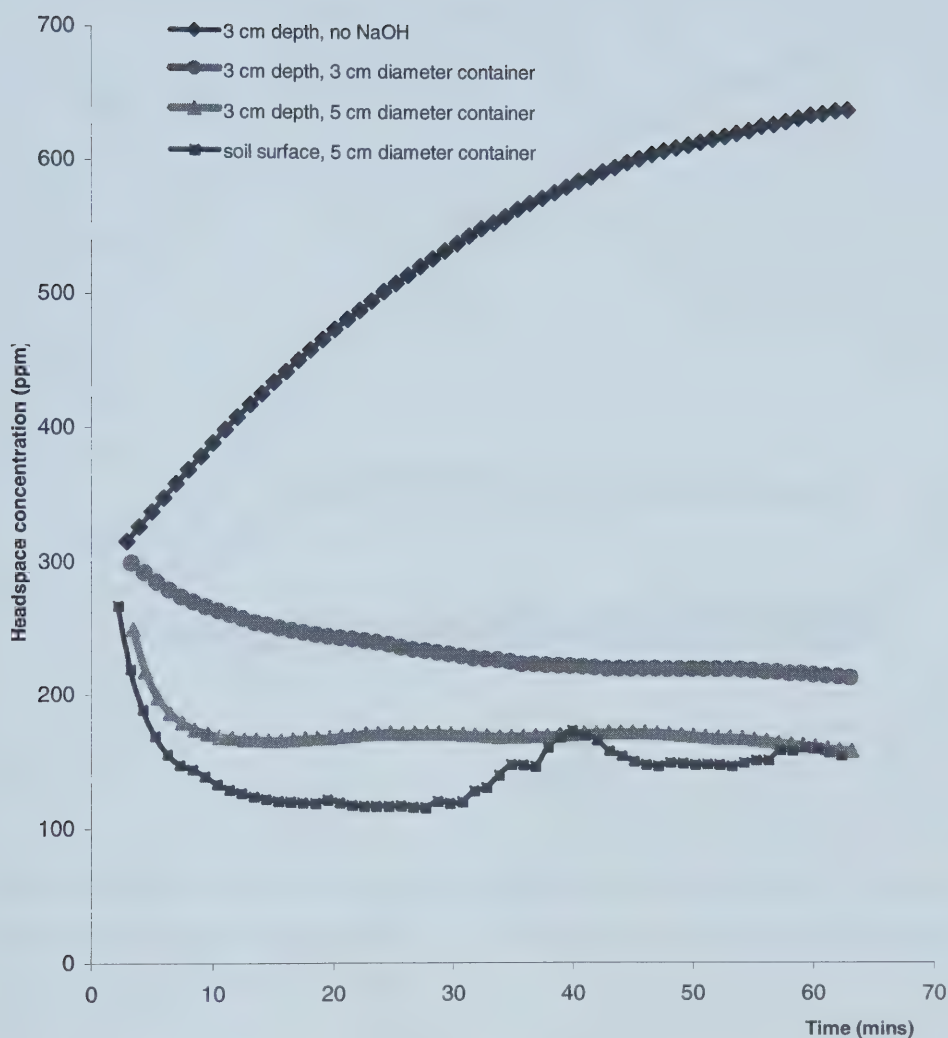


Fig. 4.3. Effect of container size on NaOH absorption under low CO₂ flux. The graph shows the headspace concentration of CO₂ in the chamber using different container sizes at different depths of insertion

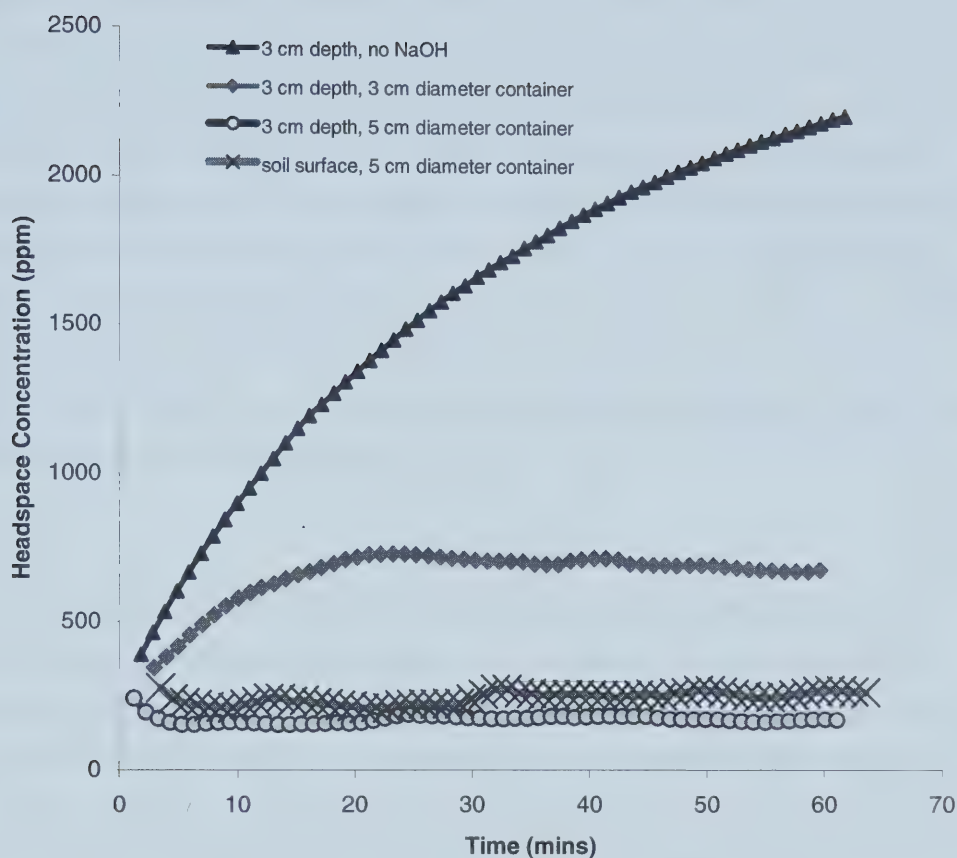


Fig. 4.4. Effect of container size on NaOH absorption under high flux. The graph shows the headspace concentration of CO_2 in the chamber using different container sizes at different depths of insertion

Contrary to the view of the proponents of the static method as being accurate, (Franzluebbers et al., 2002), at the end of the duration of the experiment, only 66.5% of the cumulative CO_2 concentration was absorbed even under low emission rates when a 3 cm container was used. When the larger diameter container was used, there was an increase in the absorption efficiency of the NaOH to 75.2%. Under high emissions the gas trap seemingly worked with better efficiency absorbing 69% of the headspace concentration in the case of the 3 cm diameter container and then 92% in the case of the 5 cm diameter container. The implication of this could be that the gas

traps are generally not very sensitive to the CO₂ gas, which the laboratory experiments suggests, or that the gas in the chamber that persists is actually due to mass flow and not just solely due to diffusion, or a combination of both factors. The results obtained from the laboratory diffusion experiments (Fig 4.2) support this assumption. The results in Figs. 4c and 4d also show that when the soil chamber was placed on the surface where CO₂ from the ambient air could easily leak around the edges (Chapter 2), there was not much difference in the pattern of CO₂ in the chamber headspace for the 5 cm diameter container. This supports the earlier view that the gas traps actually induced mass flow despite the fact that they are sensitive to the CO₂ gas (from the laboratory experiments).

4.4. CONCLUSIONS

The study showed that the gas trap was not very sensitive to the CO₂ under the controlled conditions in the laboratory and in the field, and that they could induce diffusion of gas into the chamber headspace from the soil volume not being sampled. In both the laboratory diffusion experiments and field flux measurements, there was evidence of diffusion of CO₂ gas into the chamber headspace directly related to the presence of the chemical gas traps. The effectiveness of the gas traps in absorbing the CO₂ concentration in the chamber headspace increased with the size of the container. However, a balance needs to be struck between increasing the effectiveness of absorption and curtailing mass flow. Since bulk density can have a direct effect on the phenomenon of mass flow, and based on the results of this study, the recommendation is to use smaller containers in coarser textured soil and larger ones in finer textured soils such as clays and clay loams.

The amount of gas absorbed by the chemical trap in the static chamber method involves interactions among three processes, the rate of gas emission from soils, the diffusion, or leakage of gas between the chamber headspace, through soil, and the outside atmosphere, and lastly the effectiveness of gas absorption by the trap. For the chamber used, with a 3 cm diameter NaOH trap, the rate of diffusion (0.03) is significant compared to the rate of absorption (0.09). Under low flux conditions, the rate of absorption is sufficiently high that the gas concentration in the chamber

headspace becomes lower than that of the ambient air (Fig. 4.3). This induces a concentration gradient that causes gas diffusion from the atmosphere into the chamber headspace. As a result, the gas flux measured by the static chamber method over-estimates the soil flux. Under high flux, however, the rate of absorption is not sufficient to take all the gas entering in to the chamber from the soil so that the gas concentration in the chamber headspace reaches levels significantly higher than the ambient. The concentration gradient causes diffusion from the chamber headspace into the atmosphere (leakage). As a result, the soil flux is underestimated. True, unbiased estimate of the soil flux can be obtained with the static chamber method only when the rate of absorption matches that of gas emission so that the chamber headspace concentration equals that of the ambient. In reality, this rarely occurs and, as a result, one can expect the static chamber method to be always in error.

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CHAPTER 5. CONCLUSIONS AND RECOMMENDATIONS

5.1. Study overview

The study investigated the reliability of closed chamber method for accurately estimating the flux and the factors that may undermine the accuracy of the flux estimates. The study examined the two main types of closed system chamber methods namely the static chambers (specifically those that utilized chemical traps to monitor the concentration changes in the chamber headspace) and the dynamic method using an infrared gas analyzer (LI-COR, Lincoln, Nebraska, U.S.A.) as well as some problems associated with their use. Flux estimates from the two main models often utilized to estimate flux from the headspace gas concentration namely the linear model (Denmead, 1979) and the H-M model (Hutchinson and Mosier, 1981) were compared.

5.2. The H-M model assumptions and bias

For the dynamic closed chamber method, the study found the concentration build-up in the chamber headspace to be more curvilinear than linear. For the H-M model, the condition:

$$(C_1 - C_0) / (C_2 - C_1) > 1$$

was generally not met in the first 10 minutes after the chamber placement. The fixed concentration at the upper production zone assumption of the Hutchinson and Mosier (H-M) model (1981) was not supported by the results of this study. At different depths of insertion, the value of C_d ranged from being as high as 6.4 times at 13 cm depth of insertion relative to that 3 cm depth of insertion. Although the H-M model has no recommendations for time intervals between the 3 concentration data points required for the model, this study investigated if the effect of using different time intervals on the flux estimates. The sampling time interval did not seem to greatly affect the flux estimates obtained the flux estimates obtained using the H-M model. However, the variability in the flux estimates was reduced generally using a time interval of 10 minutes or greater. Based on the results of this study, the recommended

sampling time interval is 10 minutes or greater. Contrary to the assumption of the H-M model that the placement of the chamber had very little effect on the concentration close to the upper limits of the production zone, the results of this study suggested otherwise. The study showed that the depth of insertion could have led to a redistribution of concentration in the soil profile and affected the lateral movement of gas in the soil as observed by Mathias et al. (1978). The results of this study suggest that the one-dimensional H-M model is not sufficient to account for the movement of gases across the soil-atmosphere boundary.

5.3. Comparison of linear model, H-M model and new models flux estimates

Generally, the linear model flux estimates declined linearly with sample time. However, the estimates for the first 10 minutes did not follow the expected trend as it increased instead of decreasing. This could have been due to the effect of the wind in reducing the CO₂ concentration of the surface layer of the soil. This is such that, after the placement of the chamber there is a time lag within which that layer of soil builds up in concentration enough to boost the concentration gradient between the soil and the chamber headspace to facilitate flux. This assumption is supported by results from the study by Evans et al. (1962).

Contrary to the critique of the linear model as not being reliable (Pedersen et al., 2001; Hutchinson and Mosier, 1981; Healy et al., 1996), the method of extrapolation from the linear model flux estimates as used in this study yielded reasonably good estimates of the initial flux at time zero. All the estimates derived this way were greater than 90% of that obtained using the H-M model at the various depths of insertion of the chamber. The new model developed and tested in this study performed relatively well to the H-M model flux estimates and proved to be versatile in predicting the flux under changing field conditions of diffusivity. The advantages of the new model includes:

1. Simple to use. It only requires 2 equally spaced headspace concentration measurement in order to estimate flux
2. It is versatile and allows for adjustments to the flux estimate based on the field conditions which may be very variable

3. It is an accurate way of eliminating the problem of non-linearity, which is the major setback in the use of closed chamber methods.

One precaution that must be taken in the use of this method is that the laboratory diffusion experiments must take place at the same depth of insertion as the measurement on the field.

5.4. Effect of depth of insertion on flux

Changing the depth of insertion caused an enormous distortion in the CO₂ concentration in the chamber headspace with the general trend being a greater concentration build-up at greater depths. Similar results were obtained for both the variable headspace volume and the fixed headspace volume experiments. The final CO₂ concentration in the chamber headspace at 13cm was approximately 2.25 times that at 3 cm depth of insertion. The higher fluxes obtained at greater depths of insertion could have been due to the effect of the chamber walls serving as a physical barrier to the radial diffusion of gas in the soil, thereby increasing the upward diffusion of CO₂ gas into the chamber headspace from the zone of production.

5.5. Effect of wind and atmospheric turbulence on flux

The results of the study showed that moderately high wind speeds (22.2 km/hr in this study) could lead to wide fluctuations in the headspace concentration of CO₂ even at 3 cm depth of insertion. This would especially be critical in static chambers inserted very close to the soil surface and is compounded in drier coarse-textured soils. The wind and atmospheric turbulence had a dual effect on the headspace concentration, inducing mass flow into the chamber in some instances, and in others, causing depletion. However, covering the chamber with a box during the duration of the measurement reduced the fluctuation in the headspace concentration largely and caused the concentration to build up in a more normal pattern. This study recommends therefore greater depths of insertion when measurements are taken in open fields subject to atmospheric disturbances as well as covering the chambers with a box in order to reduce the effect of the wind.

5.6. Effectiveness of NaOH gas trap as used in the static chambers

There was evidence that the gas trap (1M NaOH) used in this study induced mass flow of CO₂ into the chamber headspace as the concentration in the chamber fell below the ambient levels. The results of this study supports the critique of the static chamber method as slow and often underestimating flux. In the laboratory experiments, there was time lag between the injection of the gas and the complete depletion of the gas of 30 minutes and 50 minutes in the experiment using the 5 cm diameter and 3 cm diameter containers respectively. Under high emissions, the 5 cm diameter container absorbed 92% of the CO₂ in the chamber headspace as compared to 69% in the case of the 3 cm diameter container. Under low emissions however, the performance of the gas traps was lower, absorbing 75.2% and 66% of the headspace concentration for the 5cm and 3cm diameter containers respectively. Based on the results of this study therefore, it is recommended that a balance be struck in the choice of a suitable size for the gas traps such that it will not be too large as to induce a large occurrence of mass flow and also not too small to underestimate flux. This decision should be based on the soil properties of the site such as moisture level and texture. In addition, models used in the estimation of the flux must be adjusted to account for the time lag in absorption of the gases.

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APPENDIX A. THE LI-6400 GAS ANALYZER

A.1. The gas analyzer

A LI-6400 portable photosynthesis system (LI-COR Inc., Lincoln, Nebraska) was fitted with a CO₂ chamber (Fig. A.1). The soil surface area sampled was 71.6cm². Air was distributed in the chamber to and from the analyzer through manifolds.

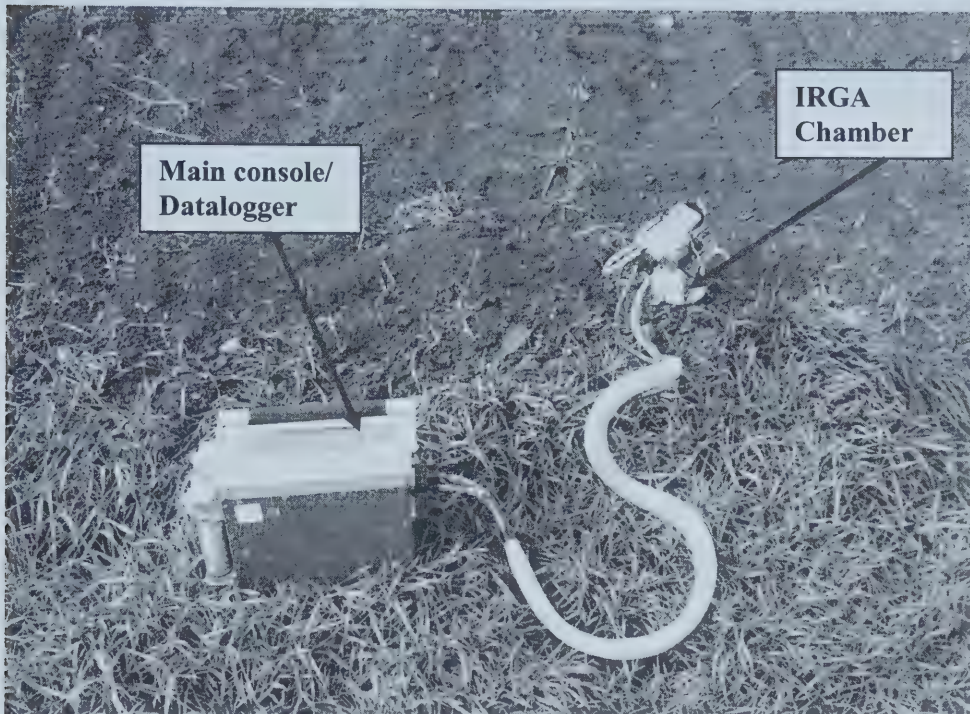


Fig. A.1. LI-6400 CO₂ gas analyzer showing the main console and soil respiration chamber

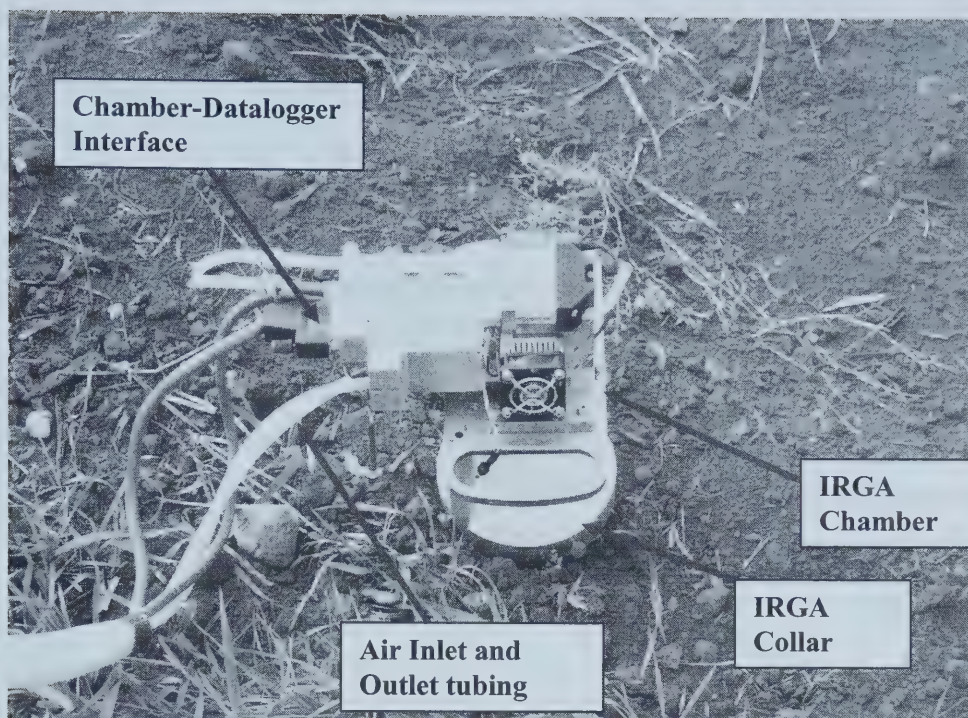


Fig. A.2. LI-6400 soil chamber showing IRGA collar

The gas analyzer mixing fan and the associated manifolds therefore achieved mixing in the chamber headspace. A high-resolution pressure sensor (Datametrics Barocel type 590, Wilmington, MA) was used to monitor the pressure inside the chamber across a range of operating conditions in order to evaluate how operation of the system may influence pressure over the soil during a typical measurement.

A.2. Taking flux measurements using the LI-6400 gas analyzer

The LI-6400 soil CO₂ flux measurement system is designed to minimize perturbations in the soil-atmosphere CO₂ concentration gradient. Before starting the measurement, the ambient CO₂ concentration at the soil surface is measured. Once the chamber is installed, the CO₂ scrubber is used to draw the CO₂ concentration in the chamber headspace down below the ambient CO₂ concentration. The scrubber is turned off, and soil CO₂ flux causes the CO₂ concentration in the chamber headspace to rise. Data are logged while the CO₂ concentration rises through the ambient level.

The software then computes the flux appropriate for the ambient concentration. The LI-6400 performs this measurement cycle automatically for as many iterations as desired.

A.3. Control of pressure fluctuations in the LI-6400 gas analyzer

A systematic bias in pressure over the soil surface can cause significant perturbations of gas exchange. Flow-through or “open” systems are problematic because the pressure differentials necessary to provide flow can suppress or enhance CO₂ emissions. In the closed system reported here, mixing in the chamber headspace is achieved with a manifold and pressure is maintained in dynamic equilibrium with ambient barometric pressure by venting the chamber through a 0.25 m length of 4 mm ID tubing.

APPENDIX B. THE ELLERSLIE RESEARCH STATION

B.1. Site Location and Climate

The Ellerslie Research station is a suburb of Edmonton located at NW-24-51-25 W4 . The climate consists of cold winters and relatively warm winters with a sub-humid moisture regime. The mean summer temperatures (May to September) is 13⁰C and the mean winter Temperature (November to March) is -9⁰C. Winter temperatures rarely fall below -40⁰C, and summer highs rarely rise above 32⁰C. The average frost-free period is 100 days. The mean annual precipitation is between 40.6 and 45.7 cm for the entire Edmonton area. The average wind velocities is less than 16km/hr and the dominant wind direction is from the North-west.

B.2. Soil type

Soils in this study area were developed on lacustrine parent material with a topography that is gently undulating. The dominant soils in the area consist of Eluviated Black Chernozems in the upper slope positions and Humic Gleysols in the depressional sites. Morphological characteristics of a sample of soils in the area is represented in the Table B.1. The landform type is a lake plain

Table B.1. Morphological characteristics of a soil profile at the Ellerslie Research station site.

Horizon	Depth (cm)	Description
L-H	13-0	Black (10YR 2/1, m), coarse and medium, pH 6.5
Ahg	0-10	Black (10YR 1.7/1, m) loam. Moderate fine granular, friable, pH 6.0
Aejg	10-18	Brownish-black (2.5Y 3/2, m) loam to silt laom, fine platey, friable, pH 5.7
Btjg	18-67	Olive-brown (2.5Y 4/3, m) clay loam, moderate fine sub-angular blocky, firm, pH 7.4
Ckg	67+	Olive-brown (2.5Y 4/3, m) clay loam, massive, slightly plastic, pH 7.4

APPENDIX C. MODEL COMPARISON RESULTS (REPLICATES)

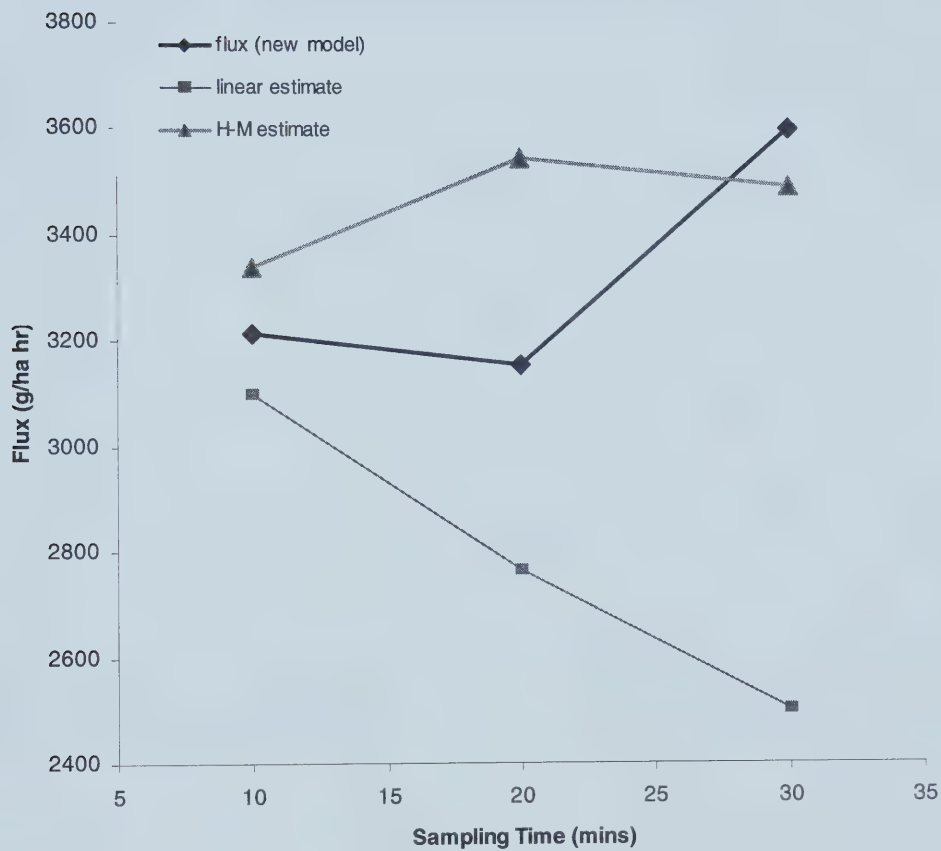


Fig. C.1. Comparison of flux estimates by linear, H-M and new models using three different sampling (rep 1).

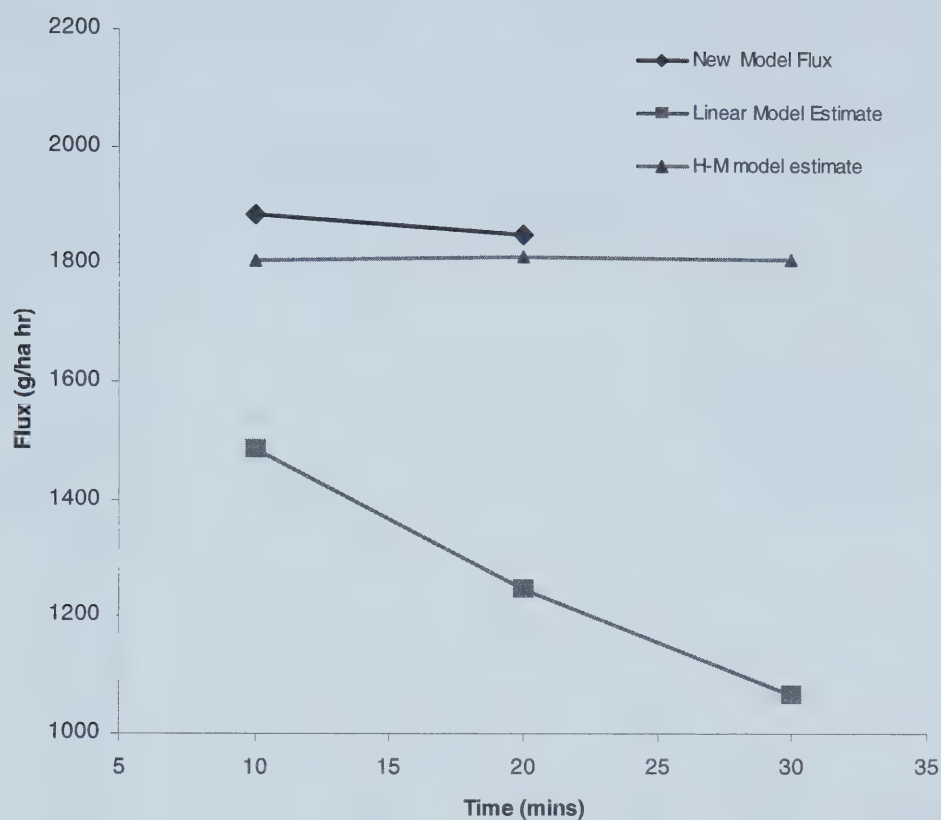


Fig. C.2. Comparison of flux estimates by linear, H-M and new models using three different sampling times (Rep 2).

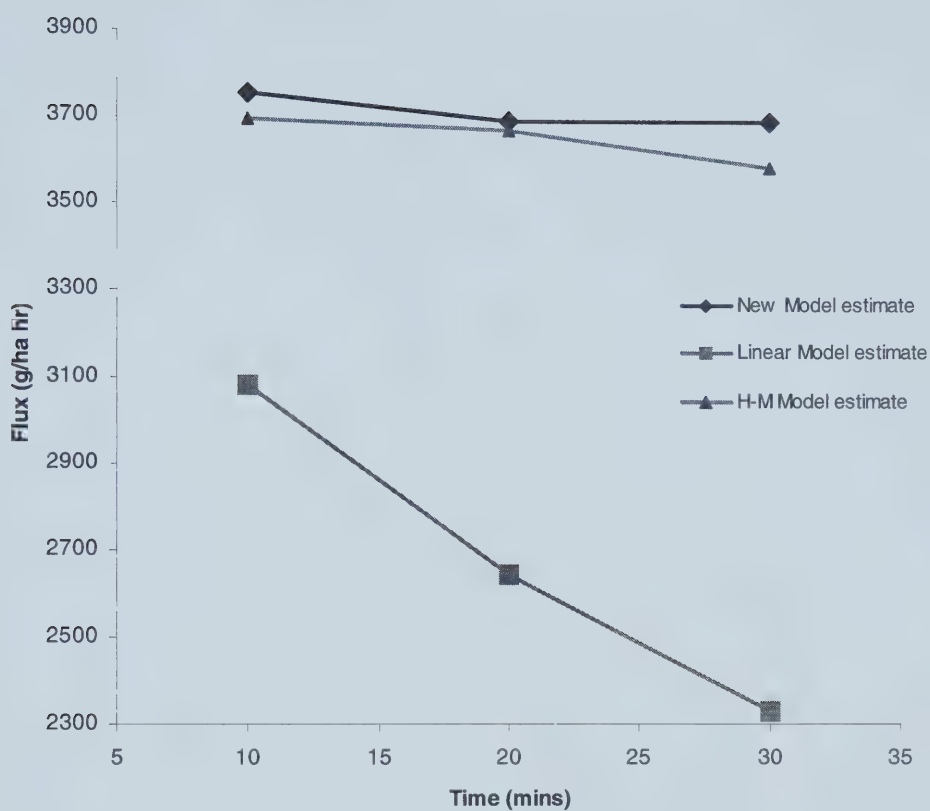


Fig. C.3. Comparison of flux estimates by linear, H-M and new models using three different sampling times (Rep 3).

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